

# NJC

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



[www.rsc.org/njc](http://www.rsc.org/njc)

## ARTICLE

# *N*-(Chalcogen)phosphorylated (chalcogen)ureas of Zinc and Cadmium(II): SSPs for Group 12-16 thin films

Cite this: DOI:

Received,  
Accepted

DOI:

www.rsc.org/

Iván D. Rojas-Montoya<sup>a</sup>, Alicia Santana-Silva<sup>a</sup>, Verónica García-Montalvo<sup>\*a</sup>, Miguel-Ángel Muñoz-Hernández<sup>\*b</sup> and Margarita Rivera<sup>c</sup>

The *bis*-chelates of zinc **7-11** and cadmium **12-17** with general formula  $[M\{R_2P(X)NC(Y)NR'\eta^2-X,Y\}_2]$  were obtained from the ligands **1-6** ( ${}^iPr_2P(X)NHC(Y)NC_4H_8$ : **1**: X = S, Y = S; **2**: X = S, Y = O; **3**: X = O, Y = S; **4**: X = S, Y = Se, **5**: X = Se, Y = S.  $Ph_2P(X)NC(Y)NC_5H_{10}$ : **6**: X = S, Y = S). **4** and cadmium complex **15** are the first examples with selenium on carbon as donor atom for this ligand system. All the compounds were characterized by FTIR and multinuclear NMR spectroscopies, and microanalysis. The molecular structures of complexes **1**, **7**, **8**, **11**, and **15** were elucidated by single crystal X-ray diffraction. TGA analysis and thermolysis experiments were carried out for the metal complexes. Selected pyrolysis residues were analyzed by SEM-EDS and XRPD. Remarkably cadmium complex **13** gave a few crystals of CdS incrustated on the surface of CdO. Preliminary studies on O,S-mixed cadmium complexes (**13** and **14**) as SSPs were carried out for the deposition of thin films via AA-CVD. The results shows CdS films from both complexes, in the case of **14** (the complex containing P=O fragment) persistent high carbon content was detected.

## Introduction

The rise of molecular nanotechnology has opened wide possibilities using the basic strategies of coordination chemistry to build up new materials and devices<sup>1</sup>. Molecular precursors are becoming a major focus of interest for both the synthesis and design of traditional and nanostructured materials. Considerable efforts have been made to synthesize and use molecular compounds as Single Source Precursors (SSPs) to obtain metal chalcogenides as thin films or nanocrystals<sup>2-4</sup>. Through SSPs it is feasible to achieve semiconductors with a wide variety of elements, combinations from Groups 12 and 16 (II-VI), 13 and 15 (III-V), 13 and 16 (III-VI), and 14 and 16 (IV-VI), which are used currently in components of satellites, TV receivers, optical fiber communications devices, compact disk players, barcode readers, full color advertising displays, solar cells, among others<sup>5</sup>. SSPs comprise a large variety of ligands,

such as seleno and thiocarbamates<sup>6-10</sup>, thiophosphinates<sup>11</sup>, silyl tellurates<sup>12</sup>, alkyl-xanthates<sup>13, 14</sup>, dithioacetylacetonates<sup>15</sup>, thio and selenocarboxylates<sup>16</sup>, thio and dithio-biuret<sup>17-22</sup> and imidodichalcogenphosphinates<sup>23, 24</sup>. The latter are very versatile ligands with general formula  $R_2P(X)NHP(Y)R_2$  (X, Y = O, S, Se, Te), that have been widely used to coordinate an extensive number of main group and transition metals<sup>25, 26</sup>.

The variation that replaces one phosphorus atom for a carbon atom,  $R_2P(X)NHC(Y)R'$  ( $LH^{X,Y}$  with X = O, S, Se; Y = O, S; R = OAlkyl, OAryl, Aryl; and R' = Alkyl, Aryl, ArylNH, AlkylNH, Alkyl<sub>2</sub>N)<sup>25, 27, 28</sup> also contain the P-N fragment and their anions have the ability to form stable metal coordination compounds<sup>25, 27-36</sup>. Some examples are the tetrahedral *bis*-chelates of Co(II), Zn(II), and Cd(II)<sup>4, 29, 30, 33</sup>, planar derivatives of Ni(II), Pd(II), and Pt(II)<sup>4, 31, 32</sup>, Lanthanide *tris*-chelates that

feature optical properties<sup>34</sup>, components of ion-selective electrodes<sup>35</sup>, and diorganotin(IV) complexes<sup>36</sup>.

Herein we report the synthesis and characterization of ligands with general formula  $R_2P(X)NHC(Y)R'$  ( $R = ^iPr$ ,  $R' =$  pyrrolidine for **1** ( $X, Y = S$ ), **2** ( $X, Y = S, O$ ), **3** ( $X, Y = O, S$ ), **4** ( $X, Y = S, Se$ ), **5** ( $X, Y = Se, S$ ) and  $R = Ph$ ,  $R' =$  piperidine for **6** ( $X, Y = S$ ) and their complexes,  $M(L^{X,Y})_2$ ;  $M = Zn(II)$ , **7-11** and  $Cd(II)$ , **12-17**. **1**, **7**, **8**, **11**, and **15** were analyzed by X-ray crystallography. **4** is the first example of this type of ligand containing  $Y = Se$ , and **15** would be the first complex with this ligand. TGA analysis and decomposition experiments in the solid state followed by FTIR were carried out for **7-17** in order to evaluate them as suitable SSPs of metal chalcogenide thin films. Preliminary thin films depositions of **13** and **14** as SSPs were performed by aerosol-assisted chemical vapor deposition (AA-CVD).

## Experimental

### Materials

All reactions were performed under an oxygen- and moisture-free argon atmosphere using standard Schlenk and glove-box techniques. Chemicals of commercial grade were purchased from Aldrich and were used as supplied. Solvents were dried by standard methods and freshly distilled prior to use.  $Ph_2P(S)Cl$ ,  $^iPr_2P(X)Cl$  ( $X = O^{37}$ ,  $S^{38}$ ,  $Se^{39}$ ),  $Ph_2P(S)NC(S)^{40}$  and  $^iPr_2P(X)NC(Y)$  ( $Y = O^{37}$ ,  $S^{40}$ ,  $Se$ ) were synthesized according to literature methods of similar compounds. The  $K[R_2P(X)NC(Y)NR']$  salts were prepared by treatment of the free ligands with potassium tert-butoxide.

### Measurement of Physical Properties

NMR data ( $^1H$ ,  $^{13}C\{^1H\}$  and  $^{31}P\{^1H\}$ ) were obtained in a Jeol-Eclipse 300 MHz and Varian-Inova 400 MHz instruments at 20 °C. Chemical shifts (ppm) are reported relative to  $SiMe_4$  for  $^1H$  and  $^{13}C$ , and 85%  $H_3PO_4$  for  $^{31}P$ . The chemical composition was determined in a Elementar Vario EL III instrument in the CHNS operation mode. The FTIR spectra were recorded in the 4000-400  $cm^{-1}$  range on a Bruker Equinox 55 Spectrometer using KBr pellets. The mass spectra were recorded in a JEOL JMS-700 instrument. The TGA and DSC analysis were obtained from a TA INSTRUMENTS SDT Q600 V8.2 BUILD 100

instrument, using a nitrogen flux of 100  $cm^3/min$ . and a temperature ramp of 10°C/min, in all cases the temperature interval was from ambient temperature to 600 °C. The pyrolysis experiments were carried out in a Thermo Scientific Thermolyne Furnace Small Benchtop Muffle. In a typical experiment 100 mg of KBr were mixed with 1 mg of the corresponding complex to make a pellet. The pellet was placed in the muffle, and the temperature was increased to a desired temperature according to the corresponding TGA, in every step a FTIR spectra was recorded. XRPD analysis was performed in a Bruker D8 ADVANCE diffractometer. SEM images were recorded in a Jeol JSM5600 LV coupled to a NORAN Energy Dispersive Spectrophotometer (EDS) working at 20 keV. Preliminary AA-CVD thin films deposits were obtained from **13** and **14**, the spray was generated in a glass airbrush connected to a quartz reaction chamber using Ar as a carrier gas. In a typical deposition  $\approx 0.2$  g of the SSP was dissolved in 40 mL of toluene, the spray was directed along the reaction chamber inside a cylindrical *Thermoline*<sup>TM</sup> 21100 furnace with a fixed temperature according to the TGA analysis (**13** at 400 °C and **14** at 500 °C). The chamber contains 10 quartz substrates (1  $cm^2$ ) on which the decomposition reactions and film depositions took place in  $\approx 15$  min. The argon flow rate was controlled by a *INFRA*<sup>TM</sup> rotameter. GAXRD analysis was performed on a Siemens D-500 diffractometer q-2q with grazing angle complement and scintillation Counter Detector.

### General synthesis procedures

**$^iPr_2P(S)NHC(S)NC_4H_8$  (1):** Pyrrolidine 3.34 mL (40 mmol) was added to a stirred solution of  $^iPr_2P(S)NC(S)$  8.28 g (40 mmol) in MeCN (60 mL). After 4 hours the solvent was removed under vacuum, dichloromethane was added, and then the compound was precipitate with hexane. The obtained white solid was filtered off and dried under vacuum. Yield: 9.43 g (90 %), M.p. 91-93 °C.  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ , 298 K, 121.65 MHz):  $\delta = 101.7$  (s).  $^1H$  NMR ( $CDCl_3$ , 300 MHz):  $\delta = 1.00-1.15$  (m, 12 H,  $CH_3-^iPr$ ), 1.83 (q, 2 H,  $CH_2$ -pyrrolidine), 1.98 (q, 2 H,  $CH_2$ -pyrrolidine), 3.33 (t, 2H,  $NCH_2$ -pyrrolidine), 3.45 (dsep, 2 H,  $CH-^iPr$ ), 3.61 (t, 2 H,  $NCH_2$ -pyrrolidine), 5.28 (s, 1 H, NH).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 298 K, 75.56 MHz):  $\delta = 17.6$  ( $CH_3-^iPr$ ), 25.0

(CH<sub>2</sub>-pyrrolidine), 26.5 (CH<sub>2</sub>-pyrrolidine), 29.3 (CH-<sup>i</sup>Pr), 48.5 (NCH<sub>2</sub>-pyrrolidine), 52.4 (NCH<sub>2</sub>-pyrrolidine), 176.2 (C=S). FTIR:  $\nu = 3364$  v(NH), 2965, 2925, 2868 v(CH), 1501, 1280, 1013 v(CN/C=S), 879, 856 v(PN), 698, 674 v(P=S). EI (m/z): 278 corresponding to <sup>i</sup>Pr<sub>2</sub>P(S)NHC(S)NC<sub>4</sub>H<sub>8</sub>. Microanalysis calculated for C<sub>11</sub>H<sub>23</sub>N<sub>2</sub>S<sub>2</sub>P: N = 10.06, C = 47.45, H = 8.33 %. Observed: N = 9.66, C = 47.19, H = 8.22 %. Crystals suitable for X-ray diffraction analysis were grown from hexane solution.

The remaining ligands (**2-6**) were obtained according to this procedure.

**<sup>i</sup>Pr<sub>2</sub>P(S)NHC(O)NC<sub>4</sub>H<sub>8</sub> (2):** Pyrrolidine 2.50 mL (30 mmol) and <sup>i</sup>Pr<sub>2</sub>P(S)NC(O) 5.73 g (30 mmol). White solid. Yield: 6.68 g (85 %), M.p. 99-101 °C. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K, 121.65 MHz):  $\delta = 94.3$  (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta = 1.10$ -1.30 (m, 12H, CH<sub>3</sub>-<sup>i</sup>Pr), 1.93 (q, 4H, CH<sub>2</sub>-pyrrolidine), 2.87 (dsep, 2H, CH-<sup>i</sup>Pr), 3.33 (t, 4H, NCH<sub>2</sub>-pyrrolidine) 4.72 (s, NH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K, 75.56 MHz):  $\delta = 16.8$  (CH<sub>3</sub>-<sup>i</sup>Pr), 25.7 (CH<sub>2</sub>-pyrrolidine), 46.2 (NCH<sub>2</sub>-pyrrolidine), 29.5 (CH-<sup>i</sup>Pr), 153.1 (C=O). FTIR:  $\nu = 3158$  v(NH), 2874, 2928, 2963 v(CH), 1630 v(C=O), 1440 v(CN), 910, 901 v(PN), 694, 664 v(P=S). EI (m/z): 262 corresponding to <sup>i</sup>Pr<sub>2</sub>P(S)NHC(O)NC<sub>4</sub>H<sub>8</sub>. Microanalysis calculated for C<sub>11</sub>H<sub>23</sub>N<sub>2</sub>SOP: N = 10.68, C = 50.38, H = 8.77 %. Observed: N = 10.57, C = 50.06, H = 8.34 %.

**<sup>i</sup>Pr<sub>2</sub>P(O)NHC(S)NC<sub>4</sub>H<sub>8</sub> (3):** Pyrrolidine 1.58 mL (19 mmol) and <sup>i</sup>Pr<sub>2</sub>P(O)NC(S) 3.64 g (19 mmol). Yellow solid. Yield 3.98 g (80 %), M.p. 105-106 °C. NMR: <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K, 121.65 MHz):  $\delta = 65.0$  (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K, 300 MHz):  $\delta = 1.08$ -1.24 (m, 12H, CH<sub>3</sub>-<sup>i</sup>Pr), 1.88 (q, 2H, CH<sub>2</sub>-pyrrolidine), 2.01 (q, 2H, CH<sub>2</sub>-pyrrolidine), 3.10 (dsep, 2H, CH-<sup>i</sup>Pr), 3.60 (t, 2H, NCH<sub>2</sub>-pyrrolidine), 3.70 (t, 2H, NCH<sub>2</sub>-pyrrolidine), 7.11 (s, NH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K, 75.56 MHz):  $\delta = 16.5$  (CH<sub>3</sub>-<sup>i</sup>Pr), 24.9 (CH<sub>2</sub>-pyrrolidine), 27.9 (CH<sub>2</sub>-pyrrolidine), 26.9 (CH-<sup>i</sup>Pr), 49.1 (NCH<sub>2</sub>-pyrrolidine), 52.5 (NCH<sub>2</sub>-pyrrolidine), 177.0 (C=S). FTIR:  $\nu = 3088$  v(NH), 2869, 2964 v(CH), 1503, 673 v(CN/C=S), 882, 852 v(PN), 1182, 1148 v(P=O). EI (m/z): 262 corresponding to <sup>i</sup>Pr<sub>2</sub>P(O)NHC(S)NC<sub>4</sub>H<sub>8</sub>. Microanalysis calculated for (C<sub>11</sub>H<sub>23</sub>N<sub>2</sub>OSP): N = 10.68, C = 50.38, H = 8.77 %. Observed: N = 10.63, C = 50.11, H = 8.35 %.

**<sup>i</sup>Pr<sub>2</sub>P(S)NHC(Se)NC<sub>4</sub>H<sub>8</sub> (4):** Pyrrolidine 0.82 mL (10 mmol) and <sup>i</sup>Pr<sub>2</sub>P(S)NHC(Se) 2.54 g (10 mmol). White solid. Yield 2.44 g (75 %), M.p. 109-110 °C. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K, 121.65 MHz):  $\delta = 104.4$  (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K, 300 MHz):  $\delta = 1.09$ -1.25 (m, 12H, CH<sub>3</sub>-<sup>i</sup>Pr), 1.93 (q, 2H, CH<sub>2</sub>-pyrrolidine), 2.11 (q, 2H, CH<sub>2</sub>-pyrrolidine), 3.36 (t, 2H, NCH<sub>2</sub>-pyrrolidine), 3.78 (m, 2H, NCH<sub>2</sub>-pyrrolidine), 3.80 (dsep, 2H, CH-<sup>i</sup>Pr), 5.66 (s, NH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K, 75.56 MHz):  $\delta = 16.4$  (CH<sub>3</sub>-<sup>i</sup>Pr), 22.0 (CH<sub>2</sub>-pyrrolidine), 25.4 (CH<sub>2</sub>-pyrrolidine), 28.4 (CH-<sup>i</sup>Pr), 47.5 (NCH<sub>2</sub>-pyrrolidine), 54.3 (NCH<sub>2</sub>-pyrrolidine), 173.3 (s, C=Se). FTIR:  $\nu = 3342$  v(NH), 2969, 2928, 2871 v(CH), 1504, 1249, 984 v(CN/C=Se), 879, 851 v(PN), 673 v(PS). EI (m/z): 326 corresponding to <sup>i</sup>Pr<sub>2</sub>P(S)NHC(Se)NC<sub>4</sub>H<sub>8</sub>. Microanalysis calculated for (C<sub>11</sub>H<sub>23</sub>N<sub>2</sub>SSeP): N = 8.61, C = 40.61, H = 7.07 %. Observed: N = 8.90, C = 40.35, H = 6.85 %.

**<sup>i</sup>Pr<sub>2</sub>P(Se)NHC(S)NC<sub>4</sub>H<sub>8</sub> (5):** Pyrrolidine 3.36 mL (41 mmol) and <sup>i</sup>Pr<sub>2</sub>P(Se)NHC(S) 10.41 g (41 mmol). White solid. Yield 12.02 g (90 %), M.p. 86-88 °C. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K, 121.65 MHz):  $\delta = 102.4$  (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K, 300 MHz):  $\delta = 0.99$ -1.20 (m, 12H, CH<sub>3</sub>-<sup>i</sup>Pr), 1.89 (q, 2H, CH<sub>2</sub>-pyrrolidine), 2.02 (q, 2H, CH<sub>2</sub>-pyrrolidine), 3.33 (t, 2H, NCH<sub>2</sub>-pyrrolidine), 3.50 (t, 2H, NCH<sub>2</sub>-pyrrolidine), 3.60 (dsep, 2H, CH-<sup>i</sup>Pr), 5.50 (s, NH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K, 75.56 MHz):  $\delta = 18.4$  (CH<sub>3</sub>-<sup>i</sup>Pr), 24.4 (CH<sub>2</sub>-pyrrolidine), 26.4 (CH<sub>2</sub>-pyrrolidine), 29.0 (CH-<sup>i</sup>Pr), 48.5 (NCH<sub>2</sub>-pyrrolidine), 52.4 (NCH<sub>2</sub>-pyrrolidine), 176.3 (C=S). FTIR:  $\nu = 3351$  v(NH), 2966, 2929, 2870 v(CH), 1497, 1276, 1016 v(CN/C=S), 880, 858 v(PN), 488 v(P=Se). EI (m/z): 326 corresponding to <sup>i</sup>Pr<sub>2</sub>P(Se)NHC(S)NC<sub>4</sub>H<sub>8</sub>. Microanalysis calculated for (C<sub>11</sub>H<sub>23</sub>N<sub>2</sub>SeSP): N = 8.61, C = 40.61, H = 7.07 %. Observed: N = 8.66, C = 40.83, H = 6.95 %.

**Ph<sub>2</sub>P(S)NHC(S)NC<sub>5</sub>H<sub>10</sub> (6):** Piperidine 3.0 mL (30 mmol) and Ph<sub>2</sub>P(S)NC(S) 7.53 g (30 mmol). White solid. Yield: 8.64 g (80 %), M.p. 120-122 °C. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K, 121.65 MHz):  $\delta = 53.1$  (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta = 1.56$  (s (br), 6H, CH<sub>2</sub>-piperidine) 3.76 (s (br), 4H, NCH<sub>2</sub>-piperidine), 7.36-7.41 (m, 6H, CH-phenyl), 7.87-7.95 (m, 4H, CH-phenyl), 6.11 (s, 1H, NH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K, 75.56 MHz):  $\delta = 24.0$  (CH<sub>2</sub>-piperidine), 25.7 (CH<sub>2</sub>-piperidine), 49.7 (NCH<sub>2</sub>-piperidine), 128.3 (CH-

phenyl), 131.4 (CH-phenyl), 131.7 (CH-phenyl), 181.6 (C=S). FTIR:  $\nu = 3160$  v(NH), 2952-2809 v(CH), 1434, 1311, 1047 v(CN/C=S), 918 v(PN), 658, 509 v(P=S). EI (m/z): 360 corresponding to  $\text{Ph}_2\text{P(S)NHC(S)NC}_5\text{H}_{10}$ . Microanalysis calculated for ( $\text{C}_{18}\text{H}_{21}\text{PS}_2\text{N}_2$ ): N = 7.77, C = 60.00, H = 5.83 %. Observed: N = 7.53, C = 59.93, H = 5.55. %.

**[Zn{<sup>i</sup>Pr<sub>2</sub>P(S)NC(S)NC<sub>4</sub>H<sub>8</sub>- $\eta^2$ -S,S}]<sub>2</sub> (7):** 0.3 g (1.07 mmol) of **1** were added to a stirred solution of ZnEt<sub>2</sub> (0.065 g, 0.53 mmol) in 30 mL of toluene, causing vigorous gas evolution and the formation of a clear colorless solution which was stirred for 4 h. Removal of the volatiles under reduced pressure produced a cream solid, which was treated with hexane (10 mL) giving a solid precipitate in the flask, the mixture was filtrated and the filtrate evaporated to dryness yielding a white solid (0.26 g, 78 %), M.p. 138-140 °C. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K, 121.65 MHz):  $\delta = 63.3$  (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K, 300 MHz):  $\delta = 1.09$ -1.25 (m, 24H, CH<sub>3</sub>-<sup>i</sup>Pr), 1.81 (m, 8H, CH<sub>2</sub>-pyrrolidine), 2.15-2.30 (m, 4H, CH-<sup>i</sup>Pr), 3.40 (t, 4H, NCH<sub>2</sub>-pyrrolidine), 3.65 (t, 4H, NCH<sub>2</sub>-pyrrolidine). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K, 50.37 MHz):  $\delta = 17.1$  (CH<sub>3</sub>-<sup>i</sup>Pr), 25.9 (CH-<sup>i</sup>Pr), 32.1 (CH<sub>2</sub>-pyrrolidine), 32.2 (CH<sub>2</sub>-pyrrolidine), 49.2 (NCH<sub>2</sub>-pyrrolidine), 49.9 (NCH<sub>2</sub>-pyrrolidine), 171.5 (CS). FTIR:  $\nu = 2964$ , 2923, 2869 v(CH), 1498, 1248, 994 v(CN/C=S), 949, 917 v(PN), 579 v(PS). EI (m/z): 618 corresponding to  $[\text{Zn}\{\text{Pr}_2\text{P(S)NC(S)NC}_4\text{H}_8\text{-}\eta^2\text{-S,S}\}_2]$ . Microanalysis calculated for ( $\text{C}_{22}\text{H}_{44}\text{N}_4\text{S}_4\text{P}_2\text{Zn}$ ): N = 9.04, C = 42.62, H = 7.10 %. Observed: N = 8.83, C = 42.33, H = 6.67 %. Crystals suitable for X-ray diffraction analysis were grown from hexane solution.

The complexes **8** to **10** were synthesized by similar procedures.

**[Zn{<sup>i</sup>Pr<sub>2</sub>P(S)NC(O)NC<sub>4</sub>H<sub>8</sub>- $\eta^2$ -S,O}]<sub>2</sub> (8):** 0.30 g (1.14 mmol) of **2** and 0.07 g (0.57 mmol) of ZnEt<sub>2</sub>. White solid. Yield 0.21 g (65%), M.p. 91-92 °C. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K, 121.65 MHz):  $\delta = 59.7$  (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K, 300 MHz):  $\delta = 1.09$ -1.25 (m, 24H, CH<sub>3</sub>-<sup>i</sup>Pr), 1.73 (m, 8H, CH<sub>2</sub>-pyrrolidine), 1.96-2.07 (m, 4H, CH-<sup>i</sup>Pr), 3.27 (m, 8H, NCH<sub>2</sub>-pyrrolidine). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K, 50.37 MHz):  $\delta = 16.3$  (CH<sub>3</sub>-<sup>i</sup>Pr), 25.8 (CH<sub>2</sub>-pyrrolidine), 29.8 (CH-<sup>i</sup>Pr), 45.8 (NCH<sub>2</sub>-pyrrolidine), 162.0 (CO). FTIR:  $\nu = 2960$ , 2870 v(CH), 1470 v(CN), 930, 913 v(PN), 681, 662 v(PS). EI (m/z): 587 corresponding to  $[\text{Zn}\{\text{Pr}_2\text{P(S)NC(O)NC}_4\text{H}_8\text{-}\eta^2\text{-S,O}\}_2]$ .

$[\text{Zn}\{\text{Pr}_2\text{P(S)NC(O)NC}_4\text{H}_8\text{-}\eta^2\text{-S,O}\}_2]$ . Microanalysis calculated for ( $\text{C}_{22}\text{H}_{44}\text{N}_4\text{S}_2\text{O}_2\text{P}_2\text{Zn}$ ): N = 9.53, C = 44.94, H = 7.4 %. Observed: N = 9.22, C = 44.50, H = 6.98 %. Crystals suitable for X-ray diffraction analysis were grown from hexane solution.

**[Zn{<sup>i</sup>Pr<sub>2</sub>P(O)NC(S)NC<sub>4</sub>H<sub>8</sub>- $\eta^2$ -O,S}]<sub>2</sub> (9):** 0.30 g (1.14 mmol) of **3** with 0.07 g (0.57 mmol) of ZnEt<sub>2</sub>. Yellow solid. Yield 0.25 g (75%), M.p. 198-199 °C. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K, 121.65 MHz):  $\delta = 49.8$  (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K, 400 MHz):  $\delta = 1.05$ -1.01 (m, 12H, CH<sub>3</sub>-<sup>i</sup>Pr), 1.79 (m, 8H, CH<sub>2</sub>-pyrrolidine), 1.90 (m, 4H, CH-<sup>i</sup>Pr), 3.35 (t, 4H, NCH<sub>2</sub>-pyrrolidine), 3.62 (t, 4H, NCH<sub>2</sub>-pyrrolidine). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K, 100.74 MHz):  $\delta = 15.9$  (CH<sub>3</sub>-<sup>i</sup>Pr), 25.4 (CH<sub>2</sub>-pyrrolidine), 27.2 (CH<sub>2</sub>-pyrrolidine), 26.3 (CH-<sup>i</sup>Pr), 49.0 (NCH<sub>2</sub>-pyrrolidine), 49.5 (NCH<sub>2</sub>-pyrrolidine), 169.6 (CS). FTIR:  $\nu = 2967$ , 2869 v(CH), 1505, 1250, 987 v(CN/C=S), 948, 917 v(PN), 1074 v(PO). EI (m/z): 587 corresponding to  $[\text{Zn}\{\text{Pr}_2\text{P(O)NC(S)NC}_4\text{H}_8\text{-}\eta^2\text{-O,S}\}_2]$ . Microanalysis calculated for ( $\text{C}_{22}\text{H}_{44}\text{N}_4\text{O}_2\text{S}_2\text{P}_2\text{Zn}$ ): N = 9.53, C = 44.94, H = 7.40 %. Observed: N = 9.34, C = 44.50, H = 7.29 %.

**[Zn{<sup>i</sup>Pr<sub>2</sub>P(Se)NC(S)NC<sub>4</sub>H<sub>8</sub>- $\eta^2$ -Se,S}]<sub>2</sub> (10):** **5** 0.30 g (0.92 mmol) and ZnEt<sub>2</sub> 0.06 g (0.46 mmol). White solid. Yield 0.29 g (89%), M.p. 109-110 °C. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K, 121.65 MHz):  $\delta = 58.7$  (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K, 300 MHz):  $\delta = 1.04$ -1.25 (m, 24H, CH<sub>3</sub>-<sup>i</sup>Pr), 1.81 (m, 8H, CH<sub>2</sub>-pyrrolidine), 2.22-2.34 (m, 4H, CH-<sup>i</sup>Pr), 3.41 (t, 4H, NCH<sub>2</sub>-pyrrolidine), 3.66 (t, 4H, NCH<sub>2</sub>-pyrrolidine). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K, 75.56 MHz):  $\delta = 16.1$  (CH<sub>3</sub>-<sup>i</sup>Pr), 24.1 (CH-<sup>i</sup>Pr), 30.0 (CH<sub>2</sub>-pyrrolidine), 30.8 (CH<sub>2</sub>-pyrrolidine), 47.9 (NCH<sub>2</sub>-pyrrolidine), 48.7 (NCH<sub>2</sub>-pyrrolidine), 171.2 (CS). FTIR:  $\nu = 2964$ , 2931, 2869 v(CH), 1496, 1248, 994 v(CN/C=S), 948, 915 v(PN), 416 v(PSe). EI (m/z): 714 corresponding to  $[\text{Zn}\{\text{Pr}_2\text{P(Se)NC(S)NC}_4\text{H}_8\text{-}\eta^2\text{-Se,S}\}_2]$ . Microanalysis calculated for ( $\text{C}_{22}\text{H}_{44}\text{N}_4\text{Se}_2\text{S}_2\text{P}_2\text{Zn}$ ): N = 7.85, C = 37.03, H = 6.17 %. Observed: N = 7.42, C = 36.80, H = 5.89 %.

**[Zn{Ph<sub>2</sub>P(S)NC(S)NC<sub>5</sub>H<sub>10</sub>- $\eta^2$ -S,S}]<sub>2</sub> (11):** To an ethanolic solution of the potassium salt of **6** (0.77 g, 1.93 mmol) was added Zn(NO<sub>3</sub>)<sub>2</sub> (0.20 g, 0.96 mmol), the mixture was stirred for 4 h. After this time, the solvent was removed under reduced pressure and the solid treated with hexane (15 mL), a part of the solid was soluble in the hexane and was separated from the

mixture by cannula filtration and evaporated to dryness to give a white solid. Yield 0.61 g (82 %) M.p. 191-193.  $^{31}\text{P}$  { $^1\text{H}$ } NMR (121.65 MHz):  $\delta$  = 40.5 (s).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K, 300 MHz):  $\delta$  = 1.57(s (br.), 12H,  $\text{CH}_2$ -piperidine), 3.92 (s (br), 8H,  $\text{NCH}_2$ -piperidine), 7.32(ms, 6H, CH-phenyl), 7.76 (m, 4H,  $\text{CH}_{\text{Ar}}$ ).  $^{13}\text{C}$  { $^1\text{H}$ } NMR ( $\text{CDCl}_3$ , 298 K, 75.56 MHz):  $\delta$  = 24.7 ( $\text{CH}_2$ -piperidine), 26.17 ( $\text{CH}_2$ -piperidine), 49.8 ( $\text{NCH}_2$ -piperidine), 128.2 (CH-phenyl), 130.8(CH-phenyl), 131.3 (CH-phenyl), 174.8 (C=S). FTIR:  $\nu$  = 2933.54, 2853.40  $\nu$ (CH), 1492, 1298, 1005  $\nu$ (CN/C=S), 973  $\nu$ (PN), 580, 522, 485, 399  $\nu$ (PS). EI (m/z): 782 corresponding to  $[\text{Zn}\{\text{Ph}_2\text{P}(\text{S})\text{NC}(\text{S})\text{NC}_5\text{H}_{10}\text{-}\eta^2\text{-S,S}\}_2]$ . Microanalysis calculated for ( $\text{C}_{36}\text{H}_{40}\text{P}_2\text{N}_4\text{S}_4\text{Zn}$ ): N=7.14, C=55.08, H=5.10 %. Observed: N=6.96, C=54.83, H=5.05 %. Crystals suitable for X-ray diffraction analysis were grown from dichloromethane/hexane solution.

The remaining cadmium complexes **12-17** were achieved analogously from  $\text{CdCl}_2$ .

**[Cd{ $^i\text{Pr}_2\text{P}(\text{S})\text{NC}(\text{S})\text{NC}_4\text{H}_8\text{-}\eta^2\text{-S,S}$ }]<sub>2</sub> (12)**: Potassium salt of **1** (0.44 g, 1.4mmol) and  $\text{CdCl}_2$  (0.13 g, 0.71 mmol). White solid. Yield 0.28 g (60 %), M.p. 128-129 °C.  $^{31}\text{P}$ { $^1\text{H}$ } NMR ( $\text{CDCl}_3$ , 298 K, 121.65 MHz):  $\delta$  = 62.9 (s).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K, 300 MHz):  $\delta$  = 1.12-1.22 (m, 24H,  $\text{CH}_3\text{-}^i\text{Pr}$ ), 1.82 (m, 8H,  $\text{CH}_2$ -pyrrolidine), 2.22-2.33 (m, 4H,  $\text{CH-}^i\text{Pr}$ ), 3.40 (t, 4H,  $\text{NCH}_2$ -pyrrolidine), 3.66 (t, 4H,  $\text{NCH}_2$ -pyrrolidine).  $^{13}\text{C}$ { $^1\text{H}$ } NMR ( $\text{CDCl}_3$ , 298 K, 75.56 MHz):  $\delta$  = 16.0 ( $\text{CH}_3\text{-}^i\text{Pr}$ ), 25.0 ( $\text{CH-}^i\text{Pr}$ ), 29.3 ( $\text{CH}_2$ -pyrrolidine), 31.0 ( $\text{CH}_2$ -pyrrolidine), 48.2 ( $\text{NCH}_2$ -pyrrolidine), 49.1 ( $\text{NCH}_2$ -pyrrolidine) 170.1 (CS). FTIR:  $\nu$  = 2964, 2932, 2869  $\nu$ (CH), 1495, 1248, 992  $\nu$ (CN/C=S), 948, 915  $\nu$ (PN), 681, 656  $\nu$ (PS). EI (m/z): 667 corresponding to  $[\text{Cd}\{^i\text{Pr}_2\text{P}(\text{S})\text{NC}(\text{S})\text{NC}_4\text{H}_8\text{-}\eta^2\text{-S,S}\}_2]$ . Microanalysis calculated for ( $\text{C}_{22}\text{H}_{44}\text{N}_4\text{S}_4\text{P}_2\text{Cd}$ ): N = 8.40, C = 39.61, H = 6.60 %. Observed: N = 8.29, C = 39.42, H = 6.47 %.

**Cd{ $^i\text{Pr}_2\text{P}(\text{S})\text{NC}(\text{O})\text{NC}_4\text{H}_8\text{-}\eta^2\text{-S,O}$ }]<sub>2</sub> (13)**: Potassium salt of **2** (0.46 g, 1.52 mmol) and  $\text{CdCl}_2$  (0.14 g, 0.76 mmol). White solid. Yield 0.25 g (55%) M.p. 142-144 °C.  $^{31}\text{P}$ { $^1\text{H}$ } ( $\text{CDCl}_3$ , 298 K, 81.1 MHz):  $\delta$  = 60.9 (s).  $^1\text{H}$  ( $\text{CDCl}_3$ , 298 K, 400 MHz):  $\delta$  = 1.12-1.19 (m, 24H,  $\text{CH}_3\text{-}^i\text{Pr}$ ), 1.73 (m, 8H,  $\text{CH}_2$ -pyrrolidine), 2.06-2.11 (m, 4H,  $\text{CH-}^i\text{Pr}$ ), 3.61 (m, 8H,  $\text{NCH}_2$ -pyrrolidine).  $^{13}\text{C}$ { $^1\text{H}$ } ( $\text{CDCl}_3$ , 298 K, 50.37 MHz):  $\delta$  = 16.7 ( $\text{CH}_3\text{-}^i\text{Pr}$ ), 25.8

( $\text{CH}_2$ -pyrrolidine), 31.0 ( $\text{CH-}^i\text{Pr}$ ), 45.6 ( $\text{NCH}_2$ -pyrrolidine), 163.7 (CO). FTIR:  $\nu$  = 2959, 2932, 2868  $\nu$ (CH), 1450  $\nu$ (CN), 930, 904  $\nu$ (PN), 681, 648  $\nu$ (PS). EI (m/z): 634 corresponding to  $[\text{Cd}\{^i\text{Pr}_2\text{P}(\text{S})\text{NC}(\text{O})\text{NC}_4\text{H}_8\text{-}\eta^2\text{-S,O}\}_2]$ . Microanalysis calculated for ( $\text{C}_{22}\text{H}_{44}\text{N}_4\text{S}_2\text{O}_2\text{P}_2\text{Cd}$ ): N = 8.82, C = 41.61, H = 6.93 %. Observed: N = 8.53 C = 41.22, H = 6.83 %.

**[Cd{ $^i\text{Pr}_2\text{P}(\text{O})\text{NC}(\text{S})\text{NC}_4\text{H}_8\text{-}\eta^2\text{-O,S}$ }]<sub>2</sub> (14)**: (0.46 g, 1.52 mmol) of the potassium salt of **3** and  $\text{CdCl}_2$  (0.14 g, 0.76 mmol). Yellow solid. Yield 0.33 g (70 %) M.p. 178-179 °C.  $^{31}\text{P}$ { $^1\text{H}$ } ( $\text{CDCl}_3$ , 298 K, 81.1 MHz):  $\delta$  = 47.9 (s).  $^1\text{H}$  ( $\text{CDCl}_3$ , 298 K, 400 MHz):  $\delta$  = 1.04-1.11 (m, 12H,  $\text{CH}_3\text{-}^i\text{Pr}$ ), 1.77-1.85 (m, 8H,  $\text{CH}_2$ -pyrrolidine), 1.87-1.95 (m, 4H,  $\text{CH-}^i\text{Pr}$ ), 3.35 (t, 4H,  $\text{NCH}_2$ -pyrrolidine), 3.65 (t, 4H,  $\text{NCH}_2$ -pyrrolidine).  $^{13}\text{C}$ { $^1\text{H}$ } ( $\text{CDCl}_3$ , 298 K, 100.74 MHz):  $\delta$  = 16.3 ( $\text{CH}_3\text{-}^i\text{Pr}$ ), 25.4 ( $\text{CH-}^i\text{Pr}$ ), 26.7 ( $\text{CH}_2$ -pyrrolidine), 27.7 ( $\text{CH}_2$ -pyrrolidine), 49.4 ( $\text{NCH}_2$ -pyrrolidine), 49.9 ( $\text{NCH}_2$ -pyrrolidine), 168.4 (CS). FTIR:  $\nu$  = 2966, 2930, 2870  $\nu$ (CH), 1511, 1249, 987  $\nu$ (CN/C=S), 945, 915  $\nu$ (PN), 1078  $\nu$ (PO). EI (m/z): 634 corresponding to  $[\text{Cd}\{^i\text{Pr}_2\text{P}(\text{O})\text{NC}(\text{S})\text{NC}_4\text{H}_8\text{-}\eta^2\text{-O,S}\}_2]$ . Microanalysis calculated for ( $\text{C}_{22}\text{H}_{44}\text{N}_4\text{O}_2\text{S}_2\text{P}_2\text{Cd}$ ): N = 8.82, C = 41.61, H = 6.93 %. Observed: N = 8.40, C = 41.58, H = 6.64 %.

**[Cd{ $^i\text{Pr}_2\text{P}(\text{S})\text{NC}(\text{Se})\text{NC}_4\text{H}_8\text{-}\eta^2\text{-S,Se}$ }]<sub>2</sub> (15)**: Potassium salt of **4** (0.44 g, 1.22 mmol) and  $\text{CdCl}_2$  (0.12 g, 0.61 mmol). White solid. Yield 0.31 g (66 %), M.p. 150-151 °C.  $^{31}\text{P}$ { $^1\text{H}$ } NMR ( $\text{CDCl}_3$ , 298 K, 81.1 MHz):  $\delta$  = 66.6 (s).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K, 400 MHz):  $\delta$  = 1.13-1.22 (m, 24H,  $\text{CH}_3\text{-}^i\text{Pr}$ ), 1.81-1.86 (m, 8H,  $\text{CH}_2$ -pyrrolidine), 2.32-2.42 (m, 4H,  $\text{CH-}^i\text{Pr}$ ), 3.41 (m, 4H,  $\text{NCH}_2$ -pyrrolidine) 3.70 (t, 4H,  $\text{NCH}_2$ -pyrrolidine).  $^{13}\text{C}$ { $^1\text{H}$ } NMR ( $\text{CDCl}_3$ , 298 K, 100.74 MHz):  $\delta$  = 17.2 ( $\text{CH}_3\text{-}^i\text{Pr}$ ), 25.4 ( $\text{CH}_2$ -pyrrolidine), 31.9 ( $\text{CH-}^i\text{Pr}$ ), 49.5 ( $\text{NCH}_2$ -pyrrolidine), 51.9 ( $\text{NCH}_2$ -pyrrolidine), 163.1 (CSe). FTIR:  $\nu$  = 2963, 2932, 2868  $\nu$ (CH), 1501, 652  $\nu$ (CN/C=Se), 938, 907, 869  $\nu$ (PN), 690, 652  $\nu$ (PS). IE (m/z): 762 corresponding to  $[\text{Cd}\{^i\text{Pr}_2\text{P}(\text{S})\text{NC}(\text{Se})\text{NC}_4\text{H}_8\text{-}\eta^2\text{-S,Se}\}_2]$ . Microanalysis calculated for ( $\text{C}_{22}\text{H}_{44}\text{N}_4\text{S}_2\text{Se}_2\text{P}_2\text{Cd}$ ): N = 7.34, C = 34.63, H = 5.77 %. Observed: N = 7.01, C = 34.22, H = 5.68 %. Crystals suitable for X-ray diffraction analysis were grown from dichloromethane/hexane solution.

**[Cd{ $^i\text{Pr}_2\text{P}(\text{Se})\text{NC}(\text{S})\text{NC}_4\text{H}_8\text{-}\eta^2\text{-Se,S}$ }]<sub>2</sub> (16)**: Potassium salt of **5** (0.44 g, 1.22 mmol) and  $\text{CdCl}_2$  0.12 g (0.61

mmol). White solid. Yield 0.37 g (80 %), M.p. 94-95 °C.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 298 K, 81.1 MHz):  $\delta = 61.3$  (s).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K, 400 MHz):  $\delta = 1.09$ -1.18 (m, 24H,  $\text{CH}_3$ - $^i\text{Pr}$ ), 1.80 (m, 8H,  $\text{CH}_2$ -pyrrolidine), 2.32-2.42 (m, 4H,  $\text{CH}$ - $^i\text{Pr}$ ), 3.43 (m, 4H,  $\text{NCH}_2$ -pyrrolidine), 3.65 (m, 4H,  $\text{NCH}_2$ -pyrrolidine).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 298 K, 100.74 MHz):  $\delta = 17.9$  ( $\text{CH}_3$ - $^i\text{Pr}$ ), 25.8 ( $\text{CH}_2$ -pyrrolidine), 32.1 ( $\text{CH}$ - $^i\text{Pr}$ ), 49.3 ( $\text{NCH}_2$ -pyrrolidine), 51.2 ( $\text{NCH}_2$ -pyrrolidine), 177.7 (CS). FTIR:  $\nu = 2961, 2931, 2867$   $\nu(\text{CH})$ , 1489, 1246, 994  $\nu(\text{CN/C=S})$ , 950, 916  $\nu(\text{PN})$ , 418  $\nu(\text{PSe})$ . EI (m/z): 762 corresponding to  $[\text{Cd}\{^i\text{Pr}_2\text{P}(\text{Se})\text{NC}(\text{S})\text{NC}_4\text{H}_8\text{-}\eta^2\text{-Se}_2\text{S}\}_2]$ . Microanalysis calculated for  $(\text{C}_{22}\text{H}_{44}\text{N}_4\text{Se}_2\text{S}_2\text{P}_2\text{Cd})$ : N = 7.34, C = 34.63, H = 5.77 %. Observed: N = 7.09, C = 34.59, H = 5.37 %.

**[Cd{Ph<sub>2</sub>P(S)NC(S)NC<sub>5</sub>H<sub>10</sub>- $\eta^2$ -S,S}]<sub>2</sub> (17)**:  $\text{CdCl}_2$  (0.15 g, 0.45 mmol) and the potassium salt of **6** (0.52 g, 0.868 mmol). White solid. Yield 0.832 g (87 %), m.p. 224-226 °C.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 298 K, 121.65 MHz):  $\delta = 40.33$  (s).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K, 300 MHz):  $\delta = 1.58$  (s (br), 12H,  $\text{CH}_2$ -piperidine), 3.94 (s (br), 8H,  $\text{NCH}_2$ -piperidine), 7.41 (m, 6H,  $\text{CH}$ -phenyl), 7.87 (m, 4H,  $\text{CH}$ -phenyl).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 298 K, 75.56 MHz):  $\delta = 24.7$  ( $\text{CH}_2$ -piperidine), 26.3 ( $\text{CH}_2$ -piperidine), 47.40 ( $\text{NCH}_2$ -piperidine), 128.26 (13.05,  $\text{CH}$ -phenyl), 130.84 ( $\text{CH}$ -phenyl), 131.19 ( $\text{CH}$ -phenyl), 174.7 (C=S). FTIR:  $\nu = 2921$ -2853  $\nu(\text{CH})$ , 1495, 1278, 998  $\nu(\text{CN/C=S})$ , 969  $\nu(\text{PN})$ , 669, 580, 520  $\nu(\text{PS})$ . EI (m/z): 832 corresponding to  $[\text{Cd}\{\text{Ph}_2\text{P}(\text{S})\text{NC}(\text{S})\text{NC}_5\text{H}_{10}\text{-}\eta^2\text{-S,S}\}_2]$ . Microanalysis calculated for  $(\text{C}_{36}\text{H}_{40}\text{P}_2\text{N}_4\text{S}_4\text{Cd})$ : N=6.73, C=51.96, H=4.81 %. Observed: N = 6.55, C = 51.79, H = 4.70 %.

### X-ray Crystallographic Study

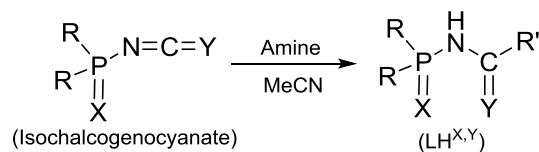
Crystals suitable for X-ray diffraction for compounds **1**, **7**, **8**, were obtained from saturated hexane solutions, while compounds **11** and **15** were crystallized from dichloromethane/hexane solutions, as described above. X-ray data were collected with a Bruker APEX CCD diffractometer with Mo-K $\alpha$  radiation. The structures were refined using the software package SHELXTL vers. 6.1<sup>41</sup>. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed into calculated positions. Absorption correction was applied with one of the following methods which is specified in CCDC's 986590-986594: multi-scan (SADABS<sup>42</sup>), psi-

scan (XPREP<sup>41</sup>), or by face indexing with XPREP and SADABS for other CCD corrections. Further details of the structure analyses are given in Table S1 of ESI. **7** and **11** showed substitutional disorder. In the case of **7** one  $^i\text{Pr}$  substituent and a Me on the other  $^i\text{Pr}$  on phosphorus atom were modelled with a 50:50% occupancy of two orientations. In **11** a phenyl substituent on phosphorus was modelled with a 58:42% occupancy of two orientations. The components of disorder in both cases were refined anisotropically applying appropriate restraints and hydrogen atoms were fixed into calculated positions with the same occupancy of disorder.

### Results and Discussion

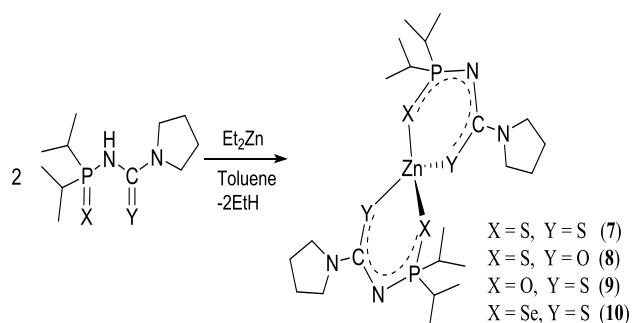
Ligands **1-5** were prepared by the reaction of the corresponding isochalcogenocyanate ( $^i\text{Pr}_2\text{P}(\text{X})\text{NC}(\text{Y})$ ): **1**: X = S, Y = S; **2**: X = S, Y = O; **3**: X = O, Y = S; **4**: X = S, Y = Se, **5**: X = Se, Y = S) with pyrrolidine, while ligand **6** was obtained by reaction of  $\text{Ph}_2\text{P}(\text{S})\text{NC}(\text{S})$  with piperidine (Scheme 1). All ligands are air stable solids except **4** and **5** which turn red after exposure to air over one day; although they can be stored under argon almost indefinitely.

Complexes of zinc **7-10** were obtained by the reaction of diethylzinc ( $\text{ZnEt}_2$ ) with the corresponding ligand (**1-3**, **5**) in toluene at ambient temperature (Scheme 2). **11-17** were prepared in ethanol at room temperature from the potassium derivatives of ligands **1-6** with  $\text{CdCl}_2$ , and for **11**  $\text{Zn}(\text{NO}_3)_2$  (Scheme 3). All complexes are air stable crystalline solids, and soluble in a variety of solvents like hexane, acetonitrile, ethanol, toluene, tetrahydrofuran and dichloromethane.

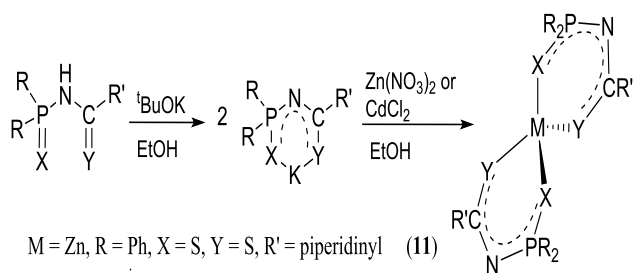


- R =  $^i\text{Pr}$ , X = S, Y = S, R' = pyrrolidinyl (**1**)  
 R =  $^i\text{Pr}$ , X = S, Y = O, R' = pyrrolidinyl (**2**)  
 R =  $^i\text{Pr}$ , X = O, Y = S, R' = pyrrolidinyl (**3**)  
 R =  $^i\text{Pr}$ , X = S, Y = Se, R' = pyrrolidinyl (**4**)  
 R =  $^i\text{Pr}$ , X = Se, Y = S, R' = pyrrolidinyl (**5**)  
 R = Ph, X = S, Y = S, R' = piperidinyl (**6**)

Scheme 1



Scheme 2



Scheme 3

### Spectroscopical and structural analysis

The FTIR spectra of ligands **1-6** show the *keto* form,  $R_2P(X)NHC(Y)R$  (X, Y = O, S, Se), as the predominant tautomer in the solid state, which is along the lines of previous reports related to similar ligands<sup>43</sup>. Accordingly the spectra exhibit absorptions at  $\approx 3226\text{ cm}^{-1}$  corresponding to the  $\nu$  (NH),  $1480\text{ cm}^{-1}$  indicative of  $\nu$ (C-N), and  $870\text{ cm}^{-1}$  which is characteristic of  $\nu$ (P-N). In the case of compounds containing N(H)–C=Y (Y = S, Se), the stretching vibration  $\nu$ (C=Y) is strongly coupled to  $\nu$ (C-N), exhibiting several absorptions that may be associated with both vibration modes<sup>44, 45</sup>. Hence **1, 3, 5, 6** show three absorptions for  $\nu$ (CN/C=Y), in the regions  $1570\text{--}1395\text{ cm}^{-1}$ ,  $1420\text{--}1260\text{ cm}^{-1}$  and  $1140\text{--}940\text{ cm}^{-1}$ , while **4** exhibits two absorptions in the regions  $1500\text{--}1400$  and  $700\text{--}600\text{ cm}^{-1}$ . The absorptions related to the  $\nu$ (C=O) and  $\nu$ (P=X) are: **2**,  $\nu$ (C=O)  $1630\text{ cm}^{-1}$ ; **3**,  $\nu$ (P=O)  $1148\text{ cm}^{-1}$ ; **1, 2, 4, and 6**,  $\nu$ (P=S)  $\approx 690\text{ cm}^{-1}$ ; and **5**,  $\nu$ (P=Se)  $488\text{ cm}^{-1}$ .

The FTIR spectra of **7-17** show the characteristic absorptions expected upon chelation of the anionic ligand through the X and Y donors to the metal center. Afterwards, the spectra feature the absence of the  $\nu$ (NH) absorption, while the shift to lower wavenumbers of the  $\nu$ (P=X) and  $\nu$ (C=Y) vibration are indicative of the M-(X,Y) coordination. In addition, both the  $\nu$ (P-N) and  $\nu$ (C-N) absorptions are shifted to higher wavelengths in agreement with an increase of bond order due to the redistribution of the electronic density around the XPNCY ring skeleton.

In the multinuclear NMR study, all signals for ligands **1-6** are consistent with the proposed *keto* tautomers.  $^1\text{H}$  NMR spectra show the resonance assigned to the NH moiety in the range  $\delta 4.72\text{--}7.11\text{ ppm}$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra show a singlet resonance that is shifted to low-field on going from O to S and Se consistent with decreased negative hyperconjugation on the phosphorus atom ( $\delta$  **3**,  $65.0\text{ ppm}$  (X = O); **1, 2, and 4**,  $\delta 94.1\text{--}101.7\text{ ppm}$  (X = S); **5**,  $\delta 102.4\text{ ppm}$  (X = Se); and **6**,  $\delta 53.1\text{ ppm}$  (X = S, R = Ph)). In the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra, the characteristic resonance of the C=Y fragment is observed at  $\delta 153.1\text{ ppm}$  for **2** (Y = O),  $\delta \approx 178.0\text{ ppm}$  for **1, 3, 5, 6** (Y = S), and  $\delta 173.3\text{ ppm}$  for **4** (Y = Se).

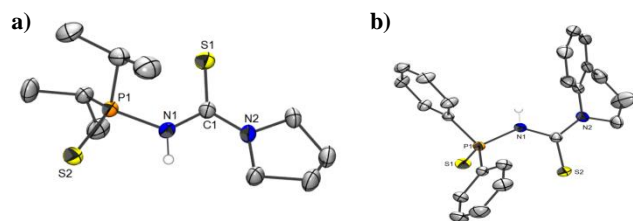
The NMR spectra of Zn (II) and Cd (II) complexes show similar features than those of the ligands. Relevant is the absence of the NH resonance signal, and that resonances are high-field shifted as result of chelate formation with concomitant electronic density redistribution along the XPNCY fragment.

Single crystals for X-ray diffraction analysis for **1** were deposited from  $\text{CH}_2\text{Cl}_2/\text{hexane}$ . Details of the crystal collection and refinement are given in Table S1 of ESI. The molecular structures along with selected bond lengths and angles are shown in Fig. 1. **1** crystallized in the monoclinic space group  $P2(1)/n$  and no significant intermolecular contacts are observed. The molecular structure confirms the results found in the FTIR and NMR spectra that the predominant tautomer, both in the solid state and solution, is the ketoamine form as reported for related  $R_2P(X)NHC(Y)R$ <sup>4, 27, 29-33</sup> ligands and imidophosphinates  $R_2P(X)NHP(Y)R_2$ <sup>26</sup>. The sulfur atoms in **1** are disposed in an *anti*-fashion and are almost coplanar to the plane subtended by the PNC moiety (deviation  $+0.27\text{ \AA}$  S1,  $-0.24\text{ \AA}$  S2). This configuration of the sulfur atoms may stem from a weak



S...H inter-molecular interaction (2.779 Å; S...N 3.501 Å) between the sulfur atom bound to the electron rich diisopropylphosphine moiety and the hydrogen on the imide fragment.

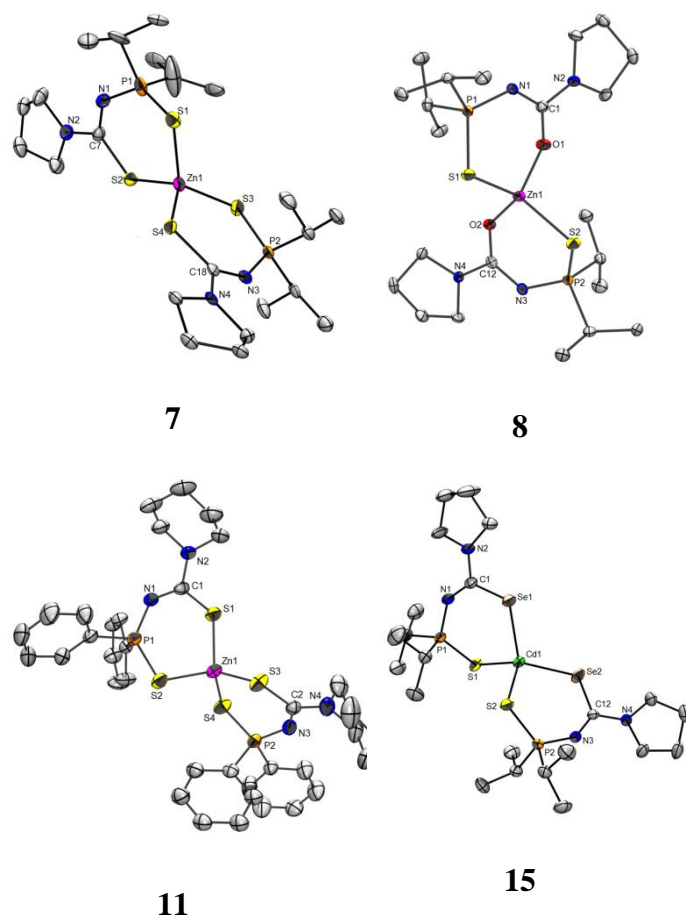
The structure of the very related ligand Ph<sub>2</sub>P(S)NHC(S)(C<sub>9</sub>H<sub>10</sub>N)<sup>40</sup> shows also an *anti*-disposition of the sulfur atoms but in this case the dihedral angle of the main planes defined by SPN atoms and SCN atoms is substantially more acute, 65° vs. 171.5° in **1**, most likely due to the additional stabilization of a weak π...π interaction of 5.470 Å between two phenyl rings on phosphorus and tetrahydroquinoline (Fig. 1). The P–S, C–S, N–P, N–C bond lengths are consistently shorter than the sum of covalent radii of the corresponding atoms (P<sub>cov</sub> = 1.07 Å, S<sub>cov</sub> = 1.05 Å, C<sub>sp2cov</sub> = 0.73 Å, N<sub>cov</sub> = 0.71 Å)<sup>46</sup>, which implies double bond character and therefore electron π delocalization along the entire SPNCSN fragment.



**Fig. 1.** Molecular structures of **1** (a) and Ph<sub>2</sub>P(S)NHC(S)(C<sub>9</sub>H<sub>10</sub>N)<sup>40</sup> (b) at the 50% probability level. Most hydrogen atoms have been omitted for clarity. The structure of (b) has been redrawn from CIF 236537. Selected bond lengths (Å) and angles (°) for **1**: P1–S2 1.9421(7), P1–N1 1.6993(15), N1–H1 0.878(18), N1–C1 1.373(2), C1–S1 1.6753(18), C1–N2 1.332(2), P1–N1–C1 130.38(12), S1–C1–N1 122.44(13), S2–P1–N1 106.31(6).

The molecular structures of **7**, **8**, **11** and **15** are depicted in Fig. 2. The coordination geometry about the metal centers is tetrahedral with mean bond angles of 110.5°, 109.4°, 109.5°, and 109.5° for **7**, **8**, **11**, and **15**, respectively. The mean bite angles are more acute as may be anticipated for the constrictions imposed by the ligand framework around the metal centers (104.9° **7**, 105.8° **8**, 108.9° **11**, and 104.1° **15**). The Zn–S bond lengths found in **7**, **8** and **11** are in the range 2.3039(9)–2.4289(12) Å, while the Zn–O bond lengths in **8** of 1.949(2) and 1.967(2) Å. They all are comparable to those in [Zn{H<sub>2</sub>NC(S)NP(S)Ph<sub>2</sub>-η<sup>2</sup>-S,S}]<sub>2</sub><sup>29</sup> and

[Zn{C<sub>6</sub>H<sub>5</sub>C(S)NP(O)O<sup>i</sup>Pr-η<sup>2</sup>-S,O}]<sub>2</sub><sup>4</sup> (mean Zn–S, Zn–O: 2.2980 Å, 1.9599 Å, respectively). **15** shows mean Cd–S and Cd–Se bond lengths of 2.5474 and 2.6097 Å, respectively, which are comparable to those found in complexes [Cd(N(SCNR<sub>2</sub>)<sub>2</sub>)<sub>2</sub>] (R = Me, Et)<sup>22</sup> and [Cd(N(<sup>i</sup>Pr<sub>2</sub>PSe)<sub>2</sub>)<sub>2</sub>]<sup>47</sup> of 2.5065 and 2.6277 Å, respectively. The bond lengths described so far are in general marginally longer than the sum of the respective covalent radii: Zn–S, 2.30 Å; Zn–O, 1.91 Å; Cd–S, 2.49 Å; Cd–Se, 2.64 Å, in accordance with single metal-chalcogen bonds<sup>46</sup>. All complexes could be described as spirocycles made of two fused six membered rings with a half-chair conformation in which the phosphorus atom is at the apex position.



**Fig. 2.** Molecular structures of **7**, **8**, **11** and **15** at the 30% probability level (hydrogen atoms have been omitted for clarity). **7**: Zn1–S1 2.3143(13), Zn1–S2 2.4289(12), Zn1–S3 2.3841(12), Zn1–S4 2.3204(12), S1–P1 2.2195(16), S2–C7 1.918(4), C7–N1 1.246(5), P1–N1 1.548(3), S1–Zn1–S2 99.78(4), S4–Zn1–S3 104.93(4), S1–Zn1–S3 124.09(4), S1–Zn1–S4 101.44(5), S2–Zn1–S3 106.27(5), S2–Zn1–S4 121.90(4), Zn1–S2–C7 118.72(14), Zn1–S1–P1 104.17(6), S1–P1–N1 125.69(15), P1–N1–C7 123.6(3). **8**: Zn1–O1 1.949(2), Zn1–S1 2.3039(9), Zn1–O2 1.967(2), Zn1–S2 2.3200(8),

O1–C1 1.287(3), S1–P1 2.0274(11), P1–N1 1.608(2), C1–N1 1.337(4), Zn1–O1–C1 128.22(19), Zn1–S1–P1 96.65(4), P1–N1–C1 126.6(2), O1–Zn1–S1 105.81(6), O2–Zn1–S2 105.69(6), O1–Zn1–O2 108.49(9), O1–Zn1–S2 110.54(7), S1–Zn1–O2 108.51(6), S1–Zn1–S2 117.55(3). **11**: Zn1–S1 2.3174(8), Zn1–S2 2.3426(8), Zn1–S3 2.3135(8), Zn1–S4 2.3381(8), S1–C1 1.745(3), S2–P1 2.0038(10), C1–N1 1.315(3), P1–N1 1.600(2), S1–Zn1–S2 108.00(3), S3–Zn1–S4 109.75(3), S1–Zn1–S3 115.40(3), S1–Zn1–S4 105.58(3), S2–Zn1–S3 104.12(3), S2–Zn1–S4 114.26(3), Zn1–S1–C1 109.46(10), Zn1–S2–P1 95.79(3), S2–P1–N1 118.35(9), P1–N1–C1 126.68(18). **15**: Cd1–Se1 2.6329(8), Cd1–S1 2.5476(15), Cd1–Se2 2.5866(9), Cd1–S2 2.5472(14), S1–P1 2.0195(18), Se1–C1 1.916(5), C1–N1 1.311(6), P1–N1 1.606(4), Se1–Cd1–S1 102.36(2), Se2–Cd1–S2 105.92(3), Se1–Cd1–S2 105.72(4), Se1–Cd1–Se2 117.25(3), S1–Cd1–S2 111.97(5), S1–Cd1–Se2 113.51(4), Se1–C1–N1 129.2(3), S1–P1–N1 118.27(16), P1–N1–C1 133.9(3).

### Thermal Behavior

Thermal analyses (TGA and DSC) in the range 25–600 °C were conducted to evaluate the thermal behavior of complexes **7–17**, and ascertain the temperature of decomposition. TGA/DSC results are tabulated in Table 1. A similar thermal behavior for all complexes was consistently observed. Thermal stability is observed until 275 °C for the Zn complexes **7–11**, and until 200 °C for those of Cd **12–17**. At higher temperature all complexes decompose cleanly with just one pathway of decomposition that ends for Zn complexes at  $\approx 400$  °C and for Cd complexes at  $\approx 375$  °C. The final residue can be associated with the corresponding metallic chalcogenides, in the case of mixed-complexes ( $ML^{X,Y}$ ), it is related with the heavier metal chalcogenides. In general, the DSC curves exhibit two principal endothermic processes. The first is the melting temperature, and the second is attributed to thermal decomposition of complexes resulting in the metal sulfides or selenides. In order to evaluate the decomposition of the proposed complexes, thermolysis in three steps was carried out using the TGA/DSC results to fix the temperature in the muffle, and FTIR spectroscopy in KBr pellets to monitor the progress of the pyrolysis. Samples were heated at  $\approx 50$  °C less than decomposition temperature; at this point the spectra only exhibit the loss of hydration water. The next measurement was recorded at the temperature observed in the thermogram which gives the maximum decomposition rate. The spectra show that almost all absorptions due to the organic vibrations have been vanished, and absorptions due to metal-chalcogen vibrations begin to rise, e.g. **8** showed a broad band at  $450\text{ cm}^{-1}$  and a weak one at  $620\text{ cm}^{-1}$  (Fig. S1). Final

experiments were done at 550 °C, the FTIR spectra show the complete absence of absorptions attributed to organic vibrations, and those due to metal-chalcogen vibrations are clearly visible, e.g. **8** v:  $1149\text{--}1039\text{ cm}^{-1}$ ,  $620$  and  $450\text{ cm}^{-1}$  (Zn–O vibrations)<sup>48–50</sup>.

SEM-EDS and XRPD analysis of the pyrolysis residues were performed for complexes **8** and **13** (S,O-mixed Zn and Cd complexes, respectively). For **8**, the chemical composition showed S (0.57 %), O (50.57%) and Zn (48.86%) giving 99% ZnO in the hexagonal habit according to XRPD pattern (Fig. S2), and it is consistent with the FTIR results. However, **13** gives a composite of CdO and CdS. Accordingly the EDS analysis shows S: 16.81%, O: 32.40 %, and Cd: 50.79 % where 58% of the sample is CdO. SEM images shown in Fig. 3 give additional evidence of this fact. In 3a the irregular material exhibits a few crystals of CdS incrustated on the surface of CdO, while 3b shows crystals of CdS. These two components were also identified by XRPD analysis (Fig. S3, cubic CdO and hexagonal CdS). The presence of oxides is attributed to handling of the sample in air. As far as we know there is no other report on the production of a mixture as the one described with two metallic chalcogenides from the same SSP. In a recent report, XPS experiments display the presence of both unoxidized and oxidized forms of iron sulfide in the as-deposited films obtained from  $Fe(SO(N(CN^iPr_2)_2)_3)$ , fact that can be ascribed to handling samples in air<sup>19</sup>.  $[Ni\{^iPr_2P(S)NP(Se)^iPr_2-\eta^2-S,S\}_2]$  leads to the deposition of films with nickel phosphide or nickel selenide depending on the deposition temperature. In the same report a heterostructure of  $Ni_{0.85}Se/Ni_2P$  was obtained by the deposition of a layer of nickel phosphide at 475 °C, followed by a nickel selenide film at 400 °C<sup>51</sup>. It is also important to note that  $[Ni\{^iPr_2P(Se)NP(Te)^iPr_2-\eta^2-Se,Te\}_2]$ <sup>52</sup> leads to the deposition of the heavier nickel chalcogenides as it was also found in  $[Ni\{^iPr_2P(S)NP(Se)^iPr_2-\eta^2-S,S\}_2]$ <sup>51</sup>. A similar behavior was observed in the zinc and cadmium sulfides films from SSPs with mixed S,O-biuret ligands<sup>22</sup>.

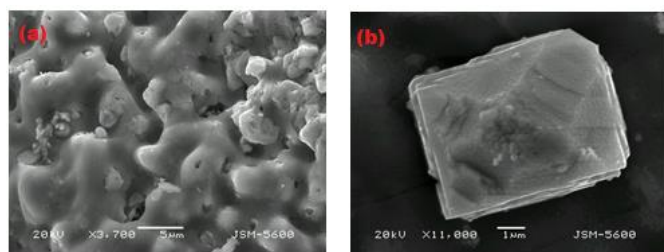
In order to assess the behavior of our O,S-mixed complexes as SSPs of thin films, we carried out preliminary studies on deposition of thin films via AACVD with **13** and **14** at 400 °C and 500 °C, respectively). The EDS analyses of both films exhibit essentially metal-enriched CdS, only the film obtained

with the ligand containing P=O (**14**) shows high carbon residue (15.71% S, 16.06% Cd and 68.21% C).

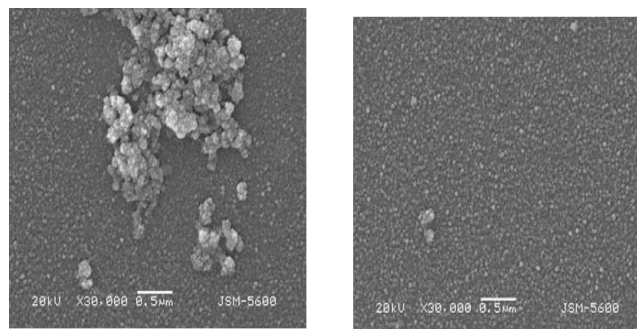
**Table 1.** TGA and DSC results for each complex.

Compound	Decomposition stage		T range of decomposition (°C)	DSC peak:	Melting point (°C)	Obtained residue (%)
	1st stage	2nd stage		T at maximum peak height (°C)		
<b>7</b>	250	350	100	310	138-140	24.60
<b>8</b>	250	350	100	284	91-92	16.77
<b>9</b>	250	475	225	313	198-199	20.68
<b>10</b>	200	450	250	323	109-110	30.88
<b>12</b>	350	400	150	354	128-129	6.42
<b>13</b>	150	350	200	306	142-144	11.49
<b>14</b>	250	500	250	325	178-179	20.66
<b>15</b>	275	375	100	335	150-151	22.88
<b>16</b>	275	475	200	320	94-95	20.82

The EDS analysis shows that the as-deposited films of **13** are composed of 45.45% S and 54.55% Cd, and corresponds to the results of the GAXRD experiment, where only the diffraction pattern of hexagonal CdS was observed (Fig. S4). SEM images (Fig. 4) of this deposit exhibit irregular clusters onto a uniform nanoparticulated surface, while the films obtained from **14** (Fig. S5) show amorphous material onto a quasi-regular nanoparticulated surface. Despite the topological imperfections observed, it is important that only CdS is obtained in contrast to the mixture achieved in the thermolysis experiments without Ar atmosphere. It also seems advantageous in order to prevent organic residues on films to use ligands with the heavier donor atom (sulfur in this case) attached to the phosphorous atom.



**Fig. 3.** SEM images of residue of cadmium compound **13**: a) Irregular Surface with CdS incrustated crystals. b) CdS crystals incrustated in the surface.



**Fig. 4.** SEM images of the as-deposited thin film from **13**. a) Cluster over a nanostructured surface. b) Uniform nanoparticulated surface.

## Conclusions

We have reported the synthesis and structures of Zn and Cd complexes **7-17**. Single-crystal X-ray structures showed in all cases bis-chelates with a distorted tetrahedral geometry around the metallic center. Ligands upon complexation gives six-membered metallacycles. TGA analysis of complexes showed in all cases a clean single-step decomposition pathway, with residues that can be related to the corresponding metallic chalcogenides. FTIR spectra of the thermolysis products at the point of maximum decomposition showed the absence of most of absorptions due to organic moieties, while absorptions due to metal-chalcogen vibrations are better resolved, this fact is also confirmed by the corresponding SEM-EDS and XRPD analysis. **13** and **14** were used as SSPs for preliminary depositions of cadmium sulfide thin films by AA-CVD. The SEM-EDS and GAXRD of films showed essentially CdS deposits. The preliminary deposition studies presented herein evidence the suitability of the proposed complexes as SSPs of nanocrystals or thin films of metal chalcogenides. Further research will be focused on this topic.

## Acknowledgements

We gratefully acknowledge support from UNAM-DGAPA (Project Grants IN201311). I. D. Rojas-Montoya is thankful to CONACyT for a PhD fellowship. We thank to Antonio Morales Espino, Mario Monroy Escamilla and Dr. Carlos R. Magaña Zavala for XRPD and SEM analyses.

## Notes and references

<sup>a</sup> Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, México D.F., 04510, México. Fax: +52(55)-56-16-22-03. E-mail: vgm@unam.mx

<sup>b</sup> Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Col. Chamilpa, Cuernavaca, Morelos C.P. 62209, México.

<sup>c</sup> Instituto de Física, Dpto. Materia Condensada, Universidad Nacional Autónoma de México, Ciudad Universitaria, México D.F. 04510, México. Electronic supplementary information (ESI) available: TGA/DSC analyses of all complexes (figs. S6). CCDC reference numbers 986590-986594 for **1**, **7**, **8**, **11** and **15**. Details of the X-ray structure analyses (Table S1). XRPD patterns of ZnO obtained from pyrolysis of **8** (fig. S2) and that of the CdO and CdS mixture obtained from pyrolysis of **13** (fig. S3). GAXRD pattern of CdS film from **13** (fig. S4). SEM images of CdS thin film obtained from **14** (fig. S5a and S5b).

- H. E. Toma, *J. Braz. Chem. Soc.*, 2003, **14**, 845-869.
- T. Trindade, P. O'Brien and X.-m. Zhang, *Chem. Mater.*, 1997, **9**, 523-530.
- A. N. Gleizes, *Chem. Vap. Deposition*, 2000, **6**, 155-173.
- D. A. Safin, A. Klein, M. G. Babashkina, H. Nöth, D. B. Krivolapov, I. A. Litvinov and H. Kozlowski, *Polyhedron*, 2009, **28**, 1504-1510.
- M. A. Malik, M. Afzaal and P. O'Brien, *Chem. Rev. (Washington, DC, U. S.)*, 2010, **110**, 4417-4446.
- D. M. Frigo, O. F. Z. Khan and P. O'Brien, *J. Cryst. Growth*, 1989, **96**, 989-992.
- M. B. Hursthouse, M. A. Malik, M. Motevalli and P. O'Brien, *Organometallics*, 1991, **10**, 730-732.
- M. B. Hursthouse, M. A. Malik, M. Motevalli and P. O'Brien, *Polyhedron*, 1992, **11**, 45-48.
- O. B. Ajayi, O. K. Osuntola, I. A. Ojo and C. Jeynes, *Thin Solid Films*, 1994, **248**, 57-62.
- C. Byrom, M. A. Malik, P. O'Brien, A. J. P. White and D. J. Williams, *Polyhedron*, 2000, **19**, 211-215.
- Y. Takahashi, R. Yuki, M. Sugiura, S. Motojima and K. Sugiyama, *J. Cryst. Growth*, 1980, **50**, 491-497.
- B. O. Dabbousi, P. J. Bonasia and J. Arnold, *J. Am. Chem. Soc.*, 1991, **113**, 3186-3188.
- D. Barreca, E. Tondello, D. Lydon, T. R. Spalding and M. Fabrizio, *Chem. Vap. Deposition*, 2003, **9**, 93-98.
- D. Barreca, A. Gasparotto, C. Maragno, E. Tondello and C. Sada, *Chem. Vap. Deposition*, 2004, **10**, 229-236.
- K. Ramasamy, M. A. Malik, P. O'Brien and J. Raftery, *Dalton Trans.*, 2009, **0**, 2196-2200.
- J. J. Vittal and M. T. Ng, *Acc. Chem. Res.*, 2006, **39**, 869-877.
- K. Ramasamy, M. A. Malik, P. O'Brien and R. J., *Mater. Res. Soc. Symp. Proc.*, 2009, **1145**, MM04-40.
- K. Ramasamy, M. A. Malik, P. O'Brien and J. Raftery, *Dalton Trans.*, 2010, **39**, 1460-1463.
- K. Ramasamy, M. A. Malik, M. Helliwell, F. Tuna and P. O'Brien, *Inorg. Chem.*, 2010, **49**, 8495-8503.
- K. Ramasamy, M. A. Malik, P. O'Brien, J. Raftery and M. Helliwell, *Chem. Mater.*, 2010, **22**, 6328-6340.
- K. Ramasamy, M. A. Malik, J. Raftery, F. Tuna and P. O'Brien, *Chem. Mater.*, 2010, **22**, 4919-4930.
- K. Ramasamy, M. A. Malik, M. Helliwell, J. Raftery and P. O'Brien, *Chem. Mater.*, 2011, **23**, 1471-1481.
- M. Afzaal, S. M. Aucott, D. Crouch, P. O'Brien, J. D. Woollins and J. H. Park, *Chem. Vap. Deposition*, 2002, **8**, 187-189.
- M. Afzaal, D. Crouch, M. A. Malik, M. Motevalli, P. O'Brien and J.-H. Park, *J. Mater. Chem.*, 2003, **13**, 639-640.
- T. Q. Ly and J. D. Woollins, *Coord. Chem. Rev.*, 1998, **176**, 451-481.
- C. Silvestru and J. E. Drake, *Coord. Chem. Rev.*, 2001, **223**, 117-216.
- F. D. Sokolov, V. V. Brusko, N. G. Zabirov and R. A. Cherkasov, *Curr. Org. Chem.*, 2006, **10**, 27-42.
- M. G. Zimin, G. A. Lazareva, N. I. Savelieva, R. G. Islamov, N. G. Zabirov, V. F. Toropova and A. N. Pudovik, *Zh. Obshch. Khim. [J. Gen. Chem. USSR]*, 1982, **52**, 1573-1581.
- F. D. Sokolov, D. A. Safin, N. G. Zabirov, V. V. Brusko, B. I. Khairutdinov, D. B. Krivolapov and I. A. Litvinov, *Eur. J. Inorg. Chem.*, 2006, **2006**, 2027-2034.
- D. A. Safin, M. G. Babashkina, F. D. Sokolov and N. G. Zabirov, *Inorg. Chem. Commun.*, 2006, **9**, 1133-1135.
- F. D. Sokolov, N. G. Zabirov, L. N. Yamalieva, V. G. Shtyrlin, R. R. Garipov, V. V. Brusko, A. Y. Verat, S. V. Baranov, P. Mlynarz, T. Glowiak and H. Kozlowski, *Inorg. Chim. Acta*, 2006, **359**, 2087-2096.
- A. Y. Verat, V. G. Shtyrlin, B. I. Khairutdinov, F. D. Sokolov, L. N. Yamalieva, D. B. Krivolapov, N. G. Zabirov, I. A. Litvinov and V. V. Klochkov, *Mendeleev Commun.*, 2008, **18**, 150-152.
- M. G. Babashkina, D. A. Safin, M. Bolte and A. Klein, *Acta Chim. Slov.*, 2010, **57**, 475-479.
- M. Borzechowska, V. Trush, I. Turowska-Tyrk, W. Amirhanov and J. Legendziewicz, *J. Alloys Compd.*, 2002, **341**, 98-106.
- L. G. Shaidarova, A. V. Gedmina, V. V. Brus'ko, N. G. Zabirov, N. A. Ulakhovich and G. K. Budnikov, *Russ. J. Appl. Chem.*, 2002, **75**, 919-925.
- O. Navrátil, E. Herrmann, N. T. T. Chau, C. Teab and J. Smola, *Collect. Czech. Chem. Commun.*, 1993, **58**, 798-805.
- T. V. Baulina, I. B. Goryunova, P. V. Petrovskii, E. I. Matrosov, E. I. Goryunov and E. E. Nifant'ev, *Dokl. Chem.*, 2006, **409**, 129-132.
- D. C. Cupertino, R. W. Keyte, A. M. Z. Slawin and J. D. Woollins, *Polyhedron*, 1998, **17**, 4219-4226.
- M. Necas, M. R. S. J. Foreman, J. Marek, J. Derek Woollins and J. Novosad, *New J. Chem.*, 2001, **25**, 1256-1263.
- V. Montiel-Palma, E. Huitrón-Rattinger, S. Cortés-Llamas, M.-Á. Muñoz-Hernández, V. García-Montalvo, E. López-Honorato and C. Silvestru, *Eur. J. Inorg. Chem.*, 2004, **2004**, 3743-3750.
- G. M. Sheldrick, SHELXTL. Version 6.0, Bruker AXS, Inc., Madison, WI, USA, 2000.
- G. M. Sheldrick, SAINT-Plus. Version 6.0, Bruker AXS, Inc., Madison, WI, USA, 2000.
- D. J. Birdsall, J. Green, T. Q. Ly, J. Novosad, M. Necas, A. M. Z. Slawin, J. D. Woollins and Z. Zak, *Eur. J. Inorg. Chem.*, 1999, 1445-1452.
- N. B. Colthup, L. H. Daly and S. E. Wiberley, *Introduction to infrared and Raman spectroscopy*, Academic Press, 1990.
- G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, Wiley, 2004.
- B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán and S. Alvarez, *Dalton Trans.*, 2008, 2832-2838.
- D. Cupertino, D. J. Birdsall, A. M. Z. Slawin and J. D. Woollins, *Inorg. Chim. Acta*, 1999, **290**, 1-7.

48. C. P. Rezende, J. B. d. Silva and N. D. S. Mohallem, *Brazilian Journal of Physics*, 2009, **39**, 248-251.
49. F. Li, Q. Li and Y. Chen, *J. Lumin.*, 2012, **132**, 2114-2121.
50. Z. Yaakob, D. Jafar Khadem, S. Shahgaldi, W. R. Wan Daud and S. M. Tasirin, *Int. J. Hydrogen Energy*, 2012, **37**, 8388-8394.
51. A. Panneerselvam, M. A. Malik, M. Afzaal, P. O'Brien and M. Helliwell, *J. Am. Chem. Soc.*, 2008, **130**, 2420-2421.
52. S. D. Robertson, T. Chivers, J. Akhtar, M. Afzaal and P. O'Brien, *Dalton Trans.*, 2008, **0**, 7004-7011.