

Dedicated to Academician Cristian Silvestru
on the occasion of his 70th anniversary

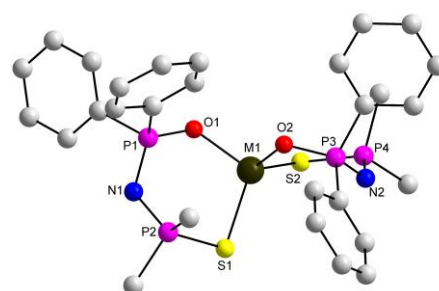
NEW ZINC AND CADMIUM COMPLEXES OF ORGANOPHOSPHORUS LIGANDS

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Group 12 metal complexes of type $M[(SPR_2)(OPR'_2)N]_2$ [$M = Zn, R = Me, R' = Ph$ (**1**); $M = Cd; R = Me, R' = Ph$ (**2**) and $M = Cd; R = Ph, R' = OEt$ (**3**)] were obtained by salt metathesis reactions. The new species were characterized in solution by multinuclear NMR spectroscopy and mass spectrometry, which show the equivalence of the two organophosphorus ligand units bonded to the metal center. For compounds $Zn[(SPMe_2)(OPPh_2)N]_2$ (**1**) and $Cd[(SPMe_2)(OPPh_2)N]_2$ (**2**) the molecular structures were determined by single crystal X-ray diffraction, when a *monometallic biconnective* coordination behavior of the $[(SPMe_2)(OPPh_2)N]^-$ ligand towards the zinc or cadmium atoms was observed. In this way a distorted tetrahedral coordination geometry around the metal was achieved. Two-dimensional supramolecular architectures were formed through weak intermolecular interactions in the crystals of the two compounds.



INTRODUCTION

The anionic organophosphorus ligands with the general formula $[(XPR_2)(YPR'_2)N]^-$ ($X, Y = O, S, Se, Te; R, R' = \text{alkyl, aryl}$) exhibit a large bite and a high flexibility. They are generally coordinated by both chalcogen atoms to the metal center,¹ in a *monometallic biconnective* way, e.g. in the previously reported group 12 complexes $Zn[(OPPh_2)_2N]_2$,² $Zn[(OPPh_2)(SePPh_2)N]_2$,³ $Zn[(SPPH_2)\{OP(OEt)_2\}N]_2$,⁴ $Hg[(EPMe_2)(SPPH_2)N]_2$ ($E = O, S$),⁵ $M[(TeP'Pr_2)_2N]_2$ ($M = Zn, Cd, Hg$),⁶ thus resulting in six-membered inorganic chelate rings ($MXYP_2N$). Other less common coordination patterns of these type

of bidentate dichalcogenoimidodiphosphinato ligands in group 12 metal complexes are: the *bimetallic triconnective* coordination, leading to twelve-membered carbon-free rings with transannular interactions, as observed in $[PhHg\{(OPR_2)(SPPH_2)N\}]_2$ ($R = Me, Ph$)⁷ and $Cd[(OPMe_2)(SPPH_2)N]_2$,⁸ the *X,N*- or *Y,N*-chelating coordination, which involves the nitrogen atom as well, as observed in $[PhHg\{OP(OPH_2)_2\}_2N]_2$,⁷ and the *X,X,Y,Y*-trimetallic *tetraconnective* coordination pattern, as found in $K[Cd_2\{(OPPh_2)_2N\}_5]$.⁸ A *monometallic monoconnective* behavior of these ligands was not observed in group 12 metal complexes.

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Besides the high flexibility, the large bite of these ligands plays also an important role in the coordination ability towards various metal centers. The XPNPY skeleton, with both phosphorus atoms having a sp^3 hybridization, are generally non-planar. Usually, a significant delocalization of the π -electrons and of the negative charge over the XPNPY skeleton was observed in the chelate rings formed by such ligands when they act as X,Y -bidentate moieties towards metals. There are known examples of compounds in which such a delocalization of the π -electrons is limited to the PNP fragment, or it is even absent.¹

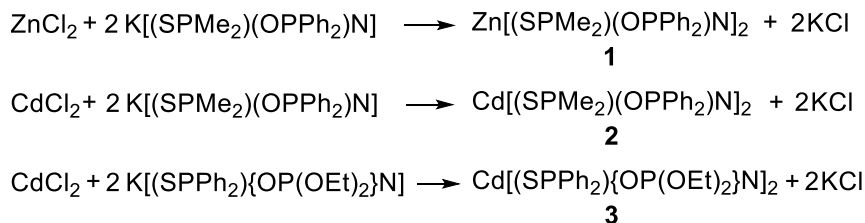
Our interest in the metal complexes with the above-described organophosphorus ligands is based not only on their interesting structural aspects, but also on their valuable applications as precursors for metal chalcogenides,^{9–11} materials for magnetic and opto-electronic devices,^{12–14} applications in catalysis¹⁵ or in biology.^{3,16–17}

The studies reported in this work are based on the interest in investigating new zinc and cadmium complexes with tetraorganodichalcogenoimidodi phosphinato ligands. Here we describe the preparation and the structural characterization of three complexes, $Zn[(SPMe_2)(OPPh_2)N]_2$ (**1**), $Cd[(SPMe_2)(OPPh_2)N]_2$

(**2**) and $Cd[(SPPH_2)\{OP(OEt)_2\}N]_2$ (**3**), as well as the molecular structures of compounds **1** and **2**, determined by single crystal X-ray diffraction studies. We must mention that complex **2** was previously reported,⁸ but it was not fully characterized.

RESULTS

The zinc and cadmium complexes of the organophosphorus ligands, $[(SPMe_2)(OPPh_2)N]^-$ and $[(SPPH_2)\{OP(OEt)_2\}N]^-$, were prepared by salt metathesis reactions between $ZnCl_2$ or $CdCl_2$ and the corresponding potassium salts, $K[(SPMe_2)(OPPh_2)N]$ and $K[(SPPH_2)\{OP(OEt)_2\}N]$, using a 1:2 molar ratio (Scheme 1). The syntheses of compounds **1** and **2** were performed in toluene, under reflux, and after the evaporation of the toluene the final products were extracted in dichloromethane. The reaction for compound **3** was carried out in dichloromethane at room temperature. All three complexes, after washing them with hexane, were isolated as air stable colorless solids, soluble in various organic solvents (dichloromethane, chloroform, dimethyl sulfoxide, methanol, acetonitrile).



Scheme 1 – Syntheses of compounds **1–3**.

The compounds were investigated by multinuclear NMR (1H , ^{13}C , ^{31}P) and mass spectrometry. The molecular structure of complexes **1** and **2** were determined by single crystal X-ray diffraction.

DISCUSSION

NMR spectroscopy and mass spectrometry

The aliphatic region of the 1H NMR spectra of **1** and **3** present the expected resonance signals specific to the protons of the methyl and ethoxy groups, respectively, attached to the phosphorus atoms. In the case of compound **1**, a doublet resonance is present due to the coupling of the

methyl protons with phosphorus, while for compound **3** the coupling with phosphorus is observed for the protons of the methylene moiety. In the aromatic region of the spectra multiplet resonance signals are observed, characteristic for the *ortho*, *meta* and *para* protons of the phenyl groups attached to phosphorus. The complexity of the resonances is due to the 1H - 1H and 1H - ^{31}P couplings of the *ortho*, *meta* and *para* protons. For compound **3** the two multiplet signals corresponding to the *meta* and *para* protons are overlapped. In the spectra the resonances are shifted when compared to the resonances for the starting potassium salts.

In the aliphatic region of the $^{13}C\{^1H\}$ NMR spectra the ^{13}C - ^{31}P couplings determine split resonances in form of doublet of doublets for **1**,

while for compound **3** two doublets are observed corresponding to the carbon atoms of the methylene and methyl groups. The aromatic region of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra show the $^{13}\text{C}\text{-}^{31}\text{P}$ couplings for the carbon atoms in the *ipso*, *ortho* and *meta* positions. For the *ipso* carbons, also the coupling with the phosphorus at a three-bond distance was observed. For compound **2**, the resonances in the multinuclear NMR spectra were identical with those previously reported,⁸ thus confirming the identity and the purity of this compound.

The presence of one set of resonances in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra confirm the equivalence in solution of the two organic groups attached to each phosphorus atom, and the equivalence of the two ligand units bonded to the metal center.

For compounds **1** and **3**, very broad singlet resonance signals can be observed (unresolved doublets) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra.

For compounds **1** and **2** the ESI+ MS spectra display the base peak corresponding to $[(\text{SPMe}_2)(\text{OPPh}_2)\text{NK}+\text{H}]^+$ cation, while for compound **3** the base peak was assigned to the $[(\text{SPPH}_2)\{\text{OP}(\text{OEt})_2\}\text{NK}+\text{K}]^+$ cation. Beside the base peaks, the molecular peaks $[\text{M}+\text{K}]^+$ were identified in the mass spectra for each complex, with intensities of 39, 55 and 75%, respectively.

Molecular structures of compounds **1** and **2**

Suitable crystals for single crystal X-ray diffraction were obtained by slow diffusion of hexane in a chloroform or dichloromethane solution, in a 1:3 or 1:1 volume ratio for compounds **1** and **2**, respectively. The ORTEP-like representation of the obtained molecular structures are shown in Fig. 1, while selected interatomic distances and bond angles are given in Table 1.

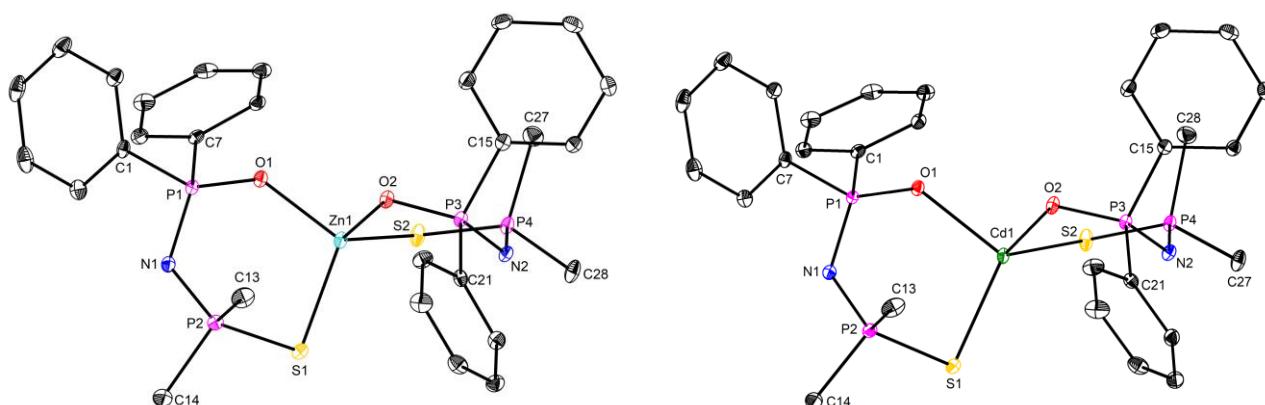


Fig. 1 – ORTEP representation with 30% probability ellipsoids for $\text{Zn}[(\text{SPMe}_2)(\text{OPPh}_2)\text{N}]_2$ (**1**) and $\text{Cd}[(\text{SPMe}_2)(\text{OPPh}_2)\text{N}]_2$ (**2**).

Table 1

Selected interatomic distances (Å) and angles (°) in compounds **1** and **2**

	1 (M=Zn)	2 (M=Cd)
M(1)–O(1)	1.9692(14)	2.1938(1)
M(1)–O(2)	1.9829(14)	2.2089(1)
M(1)–S(1)	2.3339(6)	2.4953(1)
M(1)–S(2)	2.3139(6)	2.4828(1)
P(1)–O(1)	1.5234(14)	1.5213(1)
P(3)–O(2)	1.5239(14)	1.5184(1)
P(2)–S(1)	2.0317(8)	2.0419(1)
P(4)–S(2)	2.0331(7)	2.0356(1)
N(1)–P(1)	1.5931(18)	1.5973(1)
N(1)–P(2)	1.6011(17)	1.5981(1)
N(2)–P(3)	1.5983(17)	1.6032(1)
N(2)–P(4)	1.6021(17)	1.6016(1)
O(1)–M(1)–S(1)	108.17(4)	105.02(1)
O(1)–M(1)–O(2)	102.33(6)	98.54(1)
O(1)–Zn(1)–S(2)	113.05(4)	111.29(1)
S(1)–Zn(1)–O(2)	111.59(5)	112.97(1)
S(1)–Zn(1)–S(2)	113.47(2)	124.19(1)
O(2)–Zn(1)–S(2)	107.71(4)	102.01(1)

Both compounds crystallize in the *P-1* triclinic space group. The two ligand units have a chelate *monometallic biconnective* coordination behavior, forming a distorted tetrahedral coordination geometry around the zinc or cadmium atom. The M–O and M–S bonds are very strong, the metal-chalcogen interatomic distances are very close to the sum of the covalent radii of the two elements ($\Sigma r_{\text{cov}}(\text{Zn},\text{O}) = 1.88 \text{ \AA}$, $\Sigma r_{\text{cov}}(\text{Zn},\text{S}) = 2.27 \text{ \AA}$, $\Sigma r_{\text{cov}}(\text{Cd},\text{O}) = 2.10 \text{ \AA}$, $\Sigma r_{\text{cov}}(\text{Cd},\text{S}) = 2.49 \text{ \AA}$ ¹⁸), and much smaller than the sum of the van der Waals radii of the corresponding pairs of elements ($\Sigma r_{\text{vdw}}(\text{Zn},\text{O}) = 3.89 \text{ \AA}$, $\Sigma r_{\text{vdw}}(\text{Zn},\text{S}) = 4.28 \text{ \AA}$, $\Sigma r_{\text{vdw}}(\text{Cd},\text{O}) = 3.99 \text{ \AA}$, $\Sigma r_{\text{vdw}}(\text{Cd},\text{S}) = 4.38 \text{ \AA}$ ¹⁹). None of the two hexa-atomic MOPNPS rings in each compound are planar and they have

different conformations: MO1P1N1P2S1 has a chair conformation, while MO2P3N2P4S2 has a boat conformation, in both rings the nitrogen and the metal atoms being in the apices. The P–N, P–O and P–S interatomic distances are intermediate between the simple and double bonds of the two elements, which suggests delocalization of π electrons on the OPNPS fragment. In the crystal of compounds **1** and **2** weak intermolecular O \cdots H contacts (in the range of 2.56–2.66 \AA , $\Sigma r_{\text{vdw}}(\text{O},\text{H}) = 2.70 \text{ \AA}$ ¹⁹), S \cdots H (in the range of 2.91–3.09 \AA , $\Sigma r_{\text{vdw}}(\text{S},\text{H}) = 3.09 \text{ \AA}$ ¹⁹) and $\pi\cdots\text{H}$ (in the range of 2.72–2.75 \AA , $\Sigma r_{\text{vdw}}(\pi,\text{H}) = 2.97 \text{ \AA}$ ¹⁹) interactions were observed, resulting in a 2D supramolecular architecture in both cases (Fig. 2).

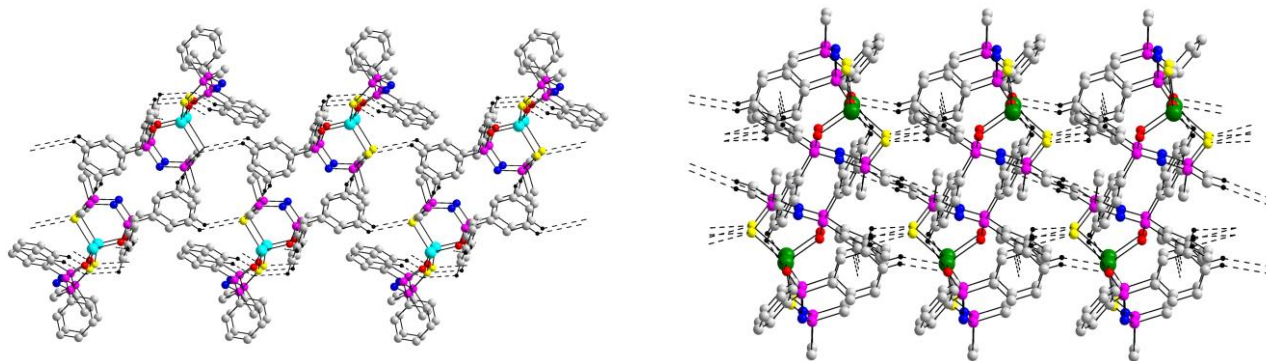


Fig. 2 – Supramolecular associations in the crystal of Zn[(SPMe₂)(OPPh₂)N]₂ (**1**, left) and Cd[(SPMe₂)(OPPh₂)N]₂ (**2**, right) (for clarity only the hydrogen atoms involved in intermolecular interactions are shown).

EXPERIMENTAL

ZnCl₂ and CdCl₂ were commercially available and used as received. The potassium salts of the organophosphorus ligands were obtained following literature procedures: K[(SPMe₂)(OPPh₂)N]²⁰ and K[(SPPPh₂){OP(OEt)₂}N]²¹. Compound **2** was prepared as reported previously.⁸ The melting point was measured on an Electrothermal 9200 apparatus and is not corrected. The multinuclear NMR spectra, including 2D experiments, were recorded for compound **1** on a BRUKER AVANCE III 400 instrument (¹H 400.13 MHz, ¹³C 100.61 MHz and ³¹P 161.97 MHz) and for compound **3** on a BRUKER AVANCE III 600 (¹H 600.13 MHz, ¹³C 150.92 MHz and ³¹P 242.92 MHz). The ¹H and ¹³C chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (ref. CHCl₃: ¹H 7.26, ¹³C 77.16 ppm). The ³¹P chemical shifts are quoted relative to H₃PO₄ (85% in water). The NMR spectra were processed using the *MestReNova* software²² and the assignments were made by using 2D correlation

experiments (H,H-COSY, H,C-HSQC and H,C-HMBC). The mass spectra were recorded on a Thermo Scientific Orbitrap XL spectrometer equipped with a standard ESI/APCI source and were processed with the *Thermo Xcalibur* software.²³

Synthesis of Zn[(SPMe₂)(OPPh₂)N]₂ (1**).** A mixture of K[(SPMe₂)(OPPh₂)N] (0.300 g, 0.864 mmol) and ZnCl₂ (0.059 g, 0.432 mmol) in toluene (50 mL) was stirred under reflux for 8 hours. Then the solvent was removed *in vacuo*, and to the resulted solid residue dichloromethane (50 mL) was added. The potassium chloride was filtered off, and the solvent was evaporated from the clear solution. The solid residue was washed with hexane and dried, and the title compound was isolated as a colorless powder. Yield: 0.264 g (90 %). M.p.: 175 °C. ¹H NMR (CDCl₃): δ 1.77 (d, 12H, SPCH₃, ²J_{PH} 13.3 Hz), 7.34 (dt, 8H, OPC₆H₅-*meta*, ³J_{HH} 7.3, ⁴J_{PH} 3.2 Hz), 7.41 (dt, 4H, OPC₆H₅-*para*, ³J_{HH} 7.3, ⁴J_{HH} 1.6 Hz), 7.77 (ddd, 8H, OPC₆H₅-*ortho*, ³J_{PH} 12.6, ³J_{HH} 7.6, ⁴J_{HH} 1.7 Hz). ¹³C{¹H} NMR (CDCl₃): δ 26.95

(dd, SPCH₃, ¹J_{PC} 74.8, ³J_{PC} 4.0 Hz), 128.24 (d, OPC₆H₅-*meta*, ³J_{PC} 12.8 Hz), 130.95 (s, br, OPC₆H₅-*para*), 131.25 (d, OPC₆H₅-*ortho*, ²J_{PC} 10.3 Hz), 136.84 (dd, OPC₆H₅-*ipso*, ¹J_{PC} 134.3, ³J_{PC} 3.7 Hz). ³¹P{¹H} NMR (CDCl₃): δ 24.74 (s, br, PO), 38.75 (s, br, PS). ESI+ MS (CH₂Cl₂+MeOH): 718.97789 (39) [M+K⁺], 348.01373 (100) [(SPMe₂)(OPPh₂)NH+K⁺].

Synthesis of Cd[(SPPH₂){OP(OEt)₂}N]₂ (3). A mixture of K[(SPPH₂){OP(OEt)₂}N] (0.200 g, 0.491 mmol) and CdCl₂ (0.045 g, 0.245 mmol) in dichloromethane (50 mL) was stirred for 43 hours at room temperature. Then the suspension was filtered, and the solvent of the filtrate was removed *in vacuo*. The obtained residue was washed with hexane and dried under reduced pressure. The title complex was isolated as a viscous, colorless compound. Yield: 0.152 g (73 %). ¹H NMR (CDCl₃): δ 1.14 (t, 12H, OCH₂CH₃, ³J_{HH} 7.1 Hz), 3.89 (dq, 8H, OCH₂CH₃, ³J_{PH} 7.2, ³J_{HH} 7.2 Hz), 7.34-7.39 (m, 12H, SPC₆H₅-*meta+para*), 7.90 (dd, 8H, SPC₆H₅-*ortho*, ³J_{PH} 14.0, ³J_{HH} 6.6 Hz). ¹³C{¹H} NMR (CDCl₃): δ 16.28 (d, OCH₂CH₃, ³J_{PC} 7.6 Hz), 62.30 (d, OCH₂CH₃, ²J_{PC} 6.0 Hz), 128.08 (d, SPC₆H₅-*meta*, ³J_{PC} 13.5 Hz), 130.73 (s, br, SPC₆H₅-*para*), 130.90 (d, SPC₆H₅-*ortho*, ²J_{PC} 11.3

Hz), 138.92 (d, br, SPC₆H₅-*ipso*, ¹J_{PC} 109.9 Hz). ³¹P{¹H} NMR (CDCl₃): δ 4.56 (s, br, PO), 34.46 (s, br, PS). ESI+ MS (MeCN): 888.99470 (75) [M+K⁺], 445.99069 (100) [(SPPH₂){OP(OEt)₂}NK+K⁺].

Crystal structure determinations

The details of the crystal structure determination and refinement for compounds **1** and **2** are given in Table 2. The crystals were mounted on MiTeGen microMounts cryoloops and data were collected at 100 or 104 K on a Bruker D8 VENTURE diffractometer using graphite-monochromated Mo-*K*_α radiation (λ = 0.71073 Å) from a IμS 3.0 microfocus source with multilayer optics. The structures were refined with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed in fixed, idealized positions and refined with a riding model and a mutual isotropic thermal parameter. The structures were solved and refined by the Bruker APEX5 software package.²⁴ Intermolecular interactions/contacts were found with PLATON.²⁵ The drawings were created with the *Diamond* program.²⁶

Table 2

X-ray crystal data and structure refinement for compounds **1** and **2**

	1	2
Empirical formula	C ₂₈ H ₃₂ N ₂ O ₂ P ₄ S ₂ Zn	C ₂₈ H ₃₂ N ₂ O ₂ P ₄ S ₂ Cd
Formula weight	680.94	728.97
Temperature (K)	100	104
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
Unit cell dimensions		
<i>a</i> (Å)	8.6046(7)	8.6551(5)
<i>b</i> (Å)	11.3915(9)	11.4691(6)
<i>c</i> (Å)	16.2449(12)	16.4330(8)
α (°)	81.022(3)	77.459(2)
β (°)	84.915(3)	84.459(2)
γ (°)	82.188(3)	81.521(2)
Volume (Å ³)	1554.5(2)	1571.39(15)
Z	2	2
Calculated density (g/cm ³)	1.455	1.541
Absorption coefficient (mm ⁻¹)	1.159	1.060
F(000)	702	740
Crystal size, mm	0.311 x 0.271 x 0.218	0.332 x 0.319 x 0.212
θ range for data collection (°)	2.07 to 26.44	2.01 to 28.38
Reflections collected	73981	86649
Independent reflections	6394 / 5410 [R(int) = 0.0568]	7845 / 7719 [R(int) = 0.0218]
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	6394 / 0 / 356	7845 / 0 / 356
Goodness-of-fit on F ²	1.030	1.089
Final R indices [I > 2σ(I)]	R1 = 0.0285, wR2 = 0.0608	R1 = 0.0158, wR2 = 0.0409
R indices (all data)	R1 = 0.0391, wR2 = 0.0649	R1 = 0.0161, wR2 = 0.0410
Largest diff. peak and hole, (e Å ⁻³)	0.884 and -0.316	0.482 and -0.268

CONCLUSIONS

New zinc and cadmium complexes were obtained using bidentate organophosphorus ligands. The complexes were characterized in solution by multinuclear NMR spectroscopy and mass spectrometry, and for Zn[(SPMe₂)(OPPh₂)N]₂ (**1**) and Cd[(SPMe₂)(OPPh₂)N]₂ (**2**) the molecular structures were obtained by single crystal X-ray diffraction. The NMR spectra revealed the equivalence of the two ligand units in each metal complex, while the solid-state structures show a *monometallic biconnective* behavior of the bidentate ligands towards the metal center, resulting in a distorted tetrahedral coordination geometry around the metal. In the crystal, two dimensional supramolecular architectures were formed through weak intermolecular O⋯H, S⋯H and π⋯H interactions.

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Supplementary material. CCDC 2449058 and CCDC 2449059 contain the supplementary crystallographic data for compounds **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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