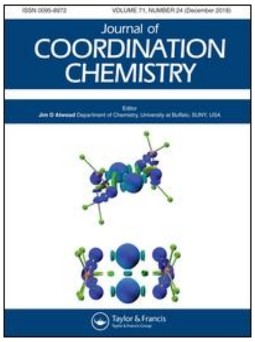

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Synthesis, characterization, and structures of zinc(II) and cadmium(II) complexes with phosphoramides bearing cyclic amino groups

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ABSTRACT
Twelve new zinc(II) and cadmium(II) complexes with symmetric ligands, $[MCl_2((R_2N)_3PO)_2]$ ($M = Zn$, R_2N = pyrrolidinyl (**1**), piperidinyl (**2**); $M = Cd$, R_2N = pyrrolidinyl (**3**), piperidinyl (**4**)), and differently substituted ligands of the general formula $[MCl_2(R_2N)PO(R'_2N)_2]$ ($M = Zn$ or Cd; R_2N = Pyrr, Pip or Mor; R'_2N = Pyrr, Pip or Mor (**5–12**) have been synthesized from reaction of zinc(II) or cadmium(II) chlorides with the ligands, giving yields of 43–76%. The complexes were characterized with multinuclear (^1H, ^{13}C and ^{31}P) NMR, conductivity, IR spectroscopy, and X-ray analyses. Complexes **1**, **3**, **11,** and **12** are comprised of two ligands coordinated to the metal center in a distorted monomeric tetrahedral arrangement. The $P=O$ bond lengths of 1.490(3) (**1**), 1.497(4) (**3**), 1.480(4) (**11**), and 1.479(5) Å (**12**) are in the order observed for analogous phosphoramide complexes. The results are compared with those reported for related chalcogen counterparts.

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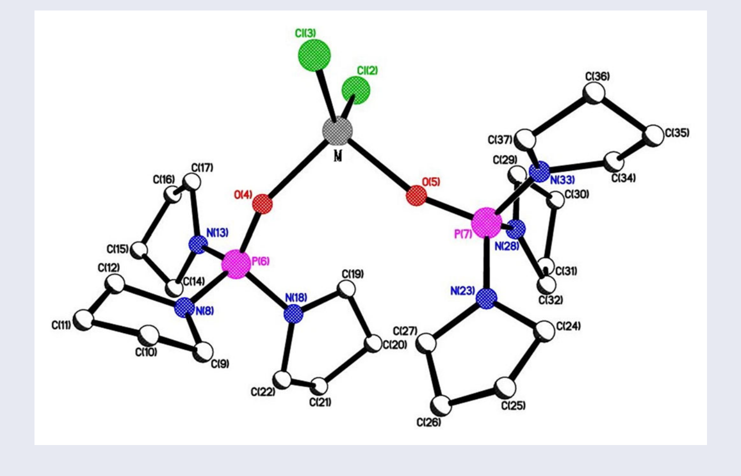


1. Introduction

Phosphoramides increasingly attract attention due to their potential applications in industry as flame retardants, in medicine as prodrugs, in catalysis and synthesis as chiral ligands [1, 2], as well as their ease of preparation, high solubility, and good reactivity toward different metal ions in many organic solvents [3–11]. The properties depend largely on the nature of substituents on the phosphorus [12]. In addition, studies into the coordination chemistry of phosphine chalcogenides R_3PE (E = O, S, Se, and Te) toward the same metal would be very informative as to the nature of metal–ligand interactions upon complex formation [13] as well as to the stereochemistry and nuclearity of the resulting complexes [14].

In this context, we have recently described the synthesis and characterization of tetrahedral metal complexes derived from bidentate piperidine containing ligands $MeN(Pip_2PE)_2$ (Pip = piperidinyl, E = S or Se) [15] and from monodentate phosphine chalcogenides *n*-Bu_3PE (E = O, S, or Se) [16]. In all these compounds, the isolated complexes exist as monomeric species. In contrast, we have shown more recently that when the ligands Pip_3PE (E = S or Se) were used, the nuclearity changed and dimers with Hg(II), Cd(II), and even Zn(II) were produced [17]. This was tentatively interpreted in terms of the presence of both the bulkier chalcogen atoms and the three piperidinyl groups in the monodentate ligand. Inspired by these results, we decided to synthesize the corresponding oxide analogues with phosphoramide ligands bearing different cyclic amino moieties including pyrrolidinyl (Pyrr), piperidinyl (Pip), and morpholinyl (Mor) groups. We were particularly interested to see how the chalcogen nature would affect the nuclearity of such complexes. The present work reports on the synthesis and characterization of new zinc(II) and cadmium(II) chloride complexes with phosphoramides $(R_2N)3PO$ (R_2N = Pyrr or Pip and $(R_2N)PO(R'_2N)_2$ (R_2N = Pyrr or Pip; R'_2N = Pyrr or Mor) using multinuclear (^1H, ^{13}C, and ^{31}P) NMR, IR spectroscopy, conductivity measurements, and X-ray analyses.

2. Experimental

2.1. General experimental procedures

Anhydrous zinc and cadmium chlorides (≥99.9%) and ethanol puriss (≥99.8%) were used as received from the commercial supplier (SIGMA-ALDRICH). All preparations were carried out under nitrogen in solvents dried by standard techniques [18] and stored over molecular sieves.

2.2. Instrumentation

All NMR spectra were recorded on a Bruker AC-300 instrument in $CDCl_3$ as solvent, ^{31}P at 121 (85% H_3PO_4), ^{1}H at 300, and ^{13}C at 75.4 MHz. IR spectra were obtained using a YL 2000 FT-IR spectrometer. The conductivity measurements were carried out for 10^{-3} M solutions of the complexes dissolved in dichloromethane (dried on molecular sieves). Phosphoramides were prepared and purified by vacuum distillation before use according to methods described [19–21].

2.3. General procedure for the preparation of variously substituted phosphoramide ligands $R_2NP(O)(R'_2N)_2$ (R_2N or R'_2N = Pip, Mor, or Pyrr)

The phosphoramides $R_2NP(O)(R'_2N)_2$ were prepared in two steps. The first step is the addition of two equivalents of the first amine (R_2NH) in anhydrous diethyl ether to a cooled solution (0 °C) of one equivalent of phosphoryl oxychloride ($POCl_3$) in the same solvent. The reaction mixture was stirred overnight at room temperature. The ammonium salt was filtered off, solvent evaporated *in vacuo* and the residue was purified by distillation to give the intermediate dichlorides, $R_2NP(O)Cl_2$. Four equivs of the second amine (R'_2NH), in diethyl ether, were then added to a cooled solution of $R_2NP(O)Cl_2$ in the same solvent. The workup was the same as in the first step. The crude materials were viscous liquids for $PyrrP(O)Pip_2$, $PipP(O)Pyrr_2$ and $MorP(O)Pyrr_2$, which were stirred at 100 °C over CaH_2 for 12 h and then purified by vacuum distillation, while the resulting solid residue $PyrrP(O)Mor_2$ was purified by recrystallization in toluene or vacuum distillation. The purity of these compounds was checked by their ^{31}P and ^{1}H NMR spectra.

2.3.1. $PipP(O)Pyrr_2$

Yield = 69%; b.p. = 135 °C/0.5 mmHg; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 2.8 (m, 12H), 1.4 (m, 8H), 1.2 (m, 6H); $\nu_{(P=O)} = 1223\ cm^{-1}$.

2.3.2. PyrrP(O)Pip2

Yield = 45%; b.p. = 138 °C/0.5 mmHg; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 3.1 (m, 12H), 1.8 (m, 4H), 1.5 (m, 12H); $\nu_{(P=O)} = 1232\ cm^{-1}$.

2.3.3. MorP(O)Pyrr2

Yield = 80%; b.p. = 150 °C/0.5 mmHg; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 3.9 (m, 4H), 3.5 (m, 12H), 2.2 (m, 8H); $\nu_{(P=O)} = 1228\ cm^{-1}$.

2.3.4. PyrrP(O)Mor2

Yield = 37%; 163 °C/0.5 mmHg ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 3.5 (m, 8H), 3.1 (m, 12H), 1.7 (m, 4H); $\nu_{(P=O)} = 1269\ cm^{-1}$.

2.4. General procedure for the preparation of 1–12

To a solution of metal chloride (1 mmol) in ethanol (20 mL) was added the ligand (2 mmol) in anhydrous dichloromethane (5 mL). The reaction mixture was stirred at room temperature for 2 h and concentrated *in vacuo*. Addition of dry diethyl ether led to precipitation of the complex, which was washed with the same solvent and vacuum dried for several hours.

2.4.1. [ZnCl2(Pyrr3PO)2] (1)

Yield = 0.30 g (45%); m. p. = 151 °C; Anal. Calcd for $C_{24}H_{48}Cl_2N_6O_2P_2Zn$: H, 7.43; C, 44.29; N, 12.91% found: H, 7.52; C, 44.01; N, 12.48%; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 3.20 (m, 12H), 1.80 (m, 12H); IR: 2979, 2881, 1462, 1348, 1251, 1211 (νP = O), 1161, 1133, 1093, 1017, 917, 873, 770, 588, 538 cm^{-1}; Λ_M ($\Omega^{-1}cm^2\ mol^{-1}$) = 9.73.

2.4.2. [ZnCl2(Pip3PO)2] (2)

Yield = 0.40 g (55%); m. p. = 206 °C; Anal. Calcd for $C_{30}H_{60}Cl_2N_6O_2P_2Zn$: H, 8.23; C, 49.02; N, 11.44% found: H, 8.86; C, 48.77; N, 11.09%; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 3.00 (m, 12H), 1.40 (m, 18H); IR: 2941, 2860, 1454, 1376, 1342, 1214 (νP = O), 1169, 1123, 1074, 1030, 959, 857, 698, 584 cm^{-1}; Λ_M ($\Omega^{-1}cm^2\ mol^{-1}$) = 6.22.

2.4.3. [CdCl2(Pyrr3PO)2] (3)

Yield = 0.49 g (70%). m. p. = 131 °C. Anal. Calcd for $C_{24}H_{48}CdCl_2N_6O_2P_2$: H, 6.93; C, 41.30; N, 12.04% found: H, 7.08; C, 41.11; N, 11.84%; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 3.10 (m, 12H), 1.70 (m, 12H); IR: 2967, 2864, 1452, 1346, 1245, 1206 (νP = O), 1141, 1086, 1014, 915, 872, 767, 588 cm^{-1}. Λ_M ($\Omega^{-1}cm^2\ mol^{-1}$) = 4.25.

2.4.4. [CdCl2(Pip3PO)2] (4)

Yield = 0.46 g (60%); Anal. Calcd for $C_{30}H_{60}CdCl_2N_6O_2P_2$: H, 7.73; C, 46.07; N, 10.75% found: H, 7.85; C, 45.93; N, 10.56%; Λ_M ($\Omega^{-1}cm^2\ mol^{-1}$) = 1.98.

2.4.5. [ZnCl2(MorP(O)Pyrr2)2] (5)

Yield = 0.52 g (76%); m. p. = 150 °C. Anal. Calcd for $C_{24}H_{48}Cl_2N_6O_4P_2Zn$: H, 7.08; C, 42.21; N, 12.32% found: H, 7.21; C, 42.08; N, 12.42%; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 3.70 (m, 4H), 3.20 (m, 12H), 1.80 (m, 8H); IR: 2975, 2858, 2187, 1452, 1265, 1211 (νP = O), 1165, 1085, 1023, 969, 909, 709, 584 cm^{-1}; Λ_M ($\Omega^{-1}cm^2\ mol^{-1}$) = 5.53.

2.4.6. [ZnCl2(PipP(O)Pyrr2)2] (6)

Yield = 0.38 g (56%); m. p. = 150 °C; Anal. Calcd for $C_{26}H_{52}Cl_2N_6O_2P_2Zn$: H, 7.72; C, 45.99; N, 12.38% found: H, 7.87; C, 46.13; N, 12.52%; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 3.52 (m, 12H), 1.87 (m, 8H), 1.32 (m, 6H); IR: 2949, 2867, 2195, 1452, 1336, 1219 (νP = O), 1148, 1195, 1013, 960, 763, 709, 573 cm^{-1}; Λ_M ($\Omega^{-1}cm^2\ mol^{-1}$) = 9.12.

2.4.7. [ZnCl2(PyrrP(O)Mor2)2] (7)

Yield = 0.52 g (73%); m. p. = 100 °C; Anal. Calcd for $C_{24}H_{48}Cl_2N_6O_6P_2Zn$: H, 6.77; C, 40.32; N, 11.76% found: H, 6.83; C, 40.57; N, 11.89%; ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 3.70 (m, 8H), 3.22 (m, 12H), 1.91 (m, 4H); IR: 2957, 2853, 1450, 1352, 1298, 1257, 1205 ($\nu P=O$), 1133, 1109, 1018, 962, 915, 726, 684, 607, 543, 476 cm^{-1}; Λ_M ($\Omega^{-1}cm^2$ mol^{-1}) = 1.36.

2.4.8. [ZnCl2(PyrrP(O)Pip2)2] (8)

Yield = 0.50 g (71%); Anal. Calcd for $C_{28}H_{56}Cl_2N_6O_2P_2Zn$: H, 7.98; C, 47.57; N, 11.89% found: H, 8.13; C, 47.63; N, 11.95%; ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 3.20 (m, 12H), 1.90 (m, 4H), 1.60 (m, 12H); Λ_M ($\Omega^{-1}cm^2$ mol^{-1}) = 11.85.

2.4.9. [CdCl2(MorP(O)Pyrr2)2] (9)

Yield = 0.49 g (67%); m. p. = 135 °C; Anal. Calcd for $C_{24}H_{48}CdCl_2N_6O_4P_2$: H, 6.63; C, 39.49; N, 11.51% found: H, 6.72; C, 39.83; N, %; ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 3.66 (m, 4H), 3.18 (m, 12H), 1.85 (m, 8H); IR: 2956, 2860, 1450, 1343, 1295, 1253, 1208 ($\nu P=O$), 1169, 1135, 1111, 1089, 1016, 969, 915, 870, 757, 702, 584, 487 cm^{-1}; Λ_M ($\Omega^{-1}cm^2$ mol^{-1}) = 1.51.

2.4.10. [CdCl2(PipP(O)Pyrr2)2] (10)

Yield = 0.50 g (69%); m. p. = 102 °C; Anal. Calcd for $C_{26}H_{52}CdCl_2N_6O_2P_2$: H, 7.22; C, 43.01; N, 11.58% found: H, 7.31; C, 43.46; N, 11.67%; ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 3.18 (m, 12H), 1.85 (m, 8H), 1.55 (m, 6H); IR: 2938, 2856, 1447, 1339, 1206 ($\nu P=O$), 1142, 1081, 1014, 957, 698, 584 cm^{-1}; Λ_M ($\Omega^{-1}cm^2$ mol^{-1}) = 4.98.

2.4.11. [CdCl2(PyrrP(O)Mor2)2] (11)

Yield = 0.34 g (43%); m. p. = 150 °C; Anal. Calcd for $C_{24}H_{48}CdCl_2N_6O_6P_2$: H, 6.35; C, 37.83; N, 11.03% found: H, 6.64; C, 38.12; N, 11.35%; ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 3.68 (m, 8H), 3.18 (m, 12H), 1.88 (m, 4H); Λ_M ($\Omega^{-1}cm^2$ mol^{-1}) = 5.80.

2.4.12. [CdCl2(PyrrP(O)Pip2)2] (12)

Yield = 0.43 g (54%); Anal. Calcd for $C_{28}H_{56}CdCl_2N_6O_2P_2$: H, 7.49; C, 44.60; N, 11.15% found: H, 7.53; C, 44.77; N, 11.27%; ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 3.22 (m, 12H), 1.86 (m, 4H), 1.58 (m, 12H); Λ_M ($\Omega^{-1}cm^2$ mol^{-1}) = 11.12.

2.5. X-ray structural details

X-ray analyses for **1** and **12** were carried out at 173 K Rigaku SCXmini CCD diffractometer with a SHINE monochromator [Mo Kα radiation ($\lambda = 0.71075$ Å)]. Data for **2** were collected at 125 K using the St Andrews Automated Robotic Diffractometer (STANDARD) [22], consisting of a Rigaku sealed-tube generator, equipped with a SHINE monochromator [Mo Kα radiation ($\lambda = 0.71075$ Å)], and a Saturn 724 CCD area detector, coupled with a Microglide goniometer head and an ACTOR SM robotic sample changer. Data for **3** were collected at 125 K using a Rigaku MM-007HF High Brilliance RA generator/confocal optics with XtaLAB P200 diffractometer [Cu Kα

Table 1. Crystal data, data collection, and refinement parameters for 1, 3, 11, and 12.

	1	3	11	12
Empirical formula	$C_{24}H_{48}Cl_2N_6O_2P_2Zn$	$C_{24}H_{48}CdCl_2N_6O_2P_2$	$C_{24}H_{48}CdCl_2N_6O_4P_2$	$C_{28}H_{56}CdCl_2N_6O_2P_2$
Formula weight	650.92	697.95	761.92	754.02
Crystal color, Habit	Colorless, Prism	Colorless, Prism	Colorless, Prism	Colorless, Prism
Crystal dimensions (mm)	0.30 × 0.17 × 0.15	0.15 × 0.06 × 0.06	0.15 × 0.15 × 0.15	0.23 × 0.18 × 0.15
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\ 2_1/c$	$P\ 2_1/c$	$C\ 2/c$	$C\ 2/c$
a (Å)	13.8006(9)	13.9491(4)	13.7860(3)	13.7783(10)
b (Å)	12.7723(8)	12.8405(4)	14.2662(2)	14.2980(10)
c (Å)	17.7204(12)	17.8032(6)	17.3730(4)	17.4136(13)
B (°)	102.907(6)	103.658(3)	108.195(2)	108.112(5)
V (Å^3)	3044.6(4)	3098.62(17)	3245.97(12)	3260.5(4)
Z	4	4	4	4
Dcalc (g/cm^3)	1.420	1.496	1.559	1.536
F (0 0 0)	1376.0	1448.00	1576	1576
Data				
Goodness-of-fit on F^2	1.081	1.088	1.092	1.053
Final R indices ($I > 2\sigma(I)$)	0.0545	0.0850	0.0517	0.0545
R indices (all data)	0.0717	0.0918	0.0554	0.0677
wR2	0.1596	0.2348	0.1576	0.1540

radiation ($\lambda = 1.54187$ Å)]. Data for **11** were collected at 173 K using a Rigaku FR-X Ultrahigh Brilliance Microfocus RA generator/confocal optics with XtaLAB P200 diffractometer [Mo Kα radiation ($\lambda = 0.71075$ Å)].

For all compounds, intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. CrystalClear [23] was used to collect all data and to process **1** and **12**, whereas CrysAlisPro [24] was used to process **3** and **11**. All data were corrected for Lorentz and polarization effects. The CrystalStructure [25] interface was used during the refinement of **1** and **3**, and Olex2 [26] for **11** and **12**.

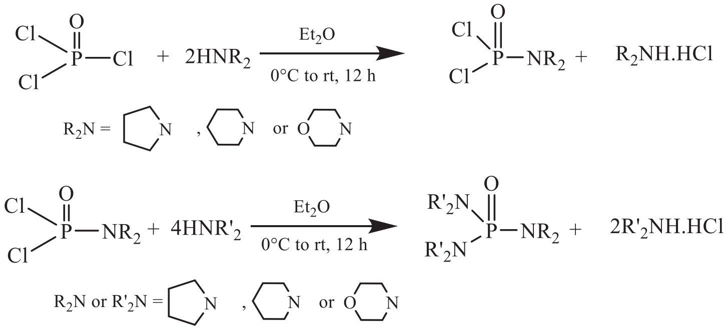
The crystal structures were all solved using dual space methods (SHELXT) [27] and refined using full matrix least square techniques (SHELEXT) [28]. All non-hydrogen atoms were refined anisotropically and hydrogens were placed geometrically using the riding model. Selected crystallographic data are presented in Table 1.

3. Results and discussion

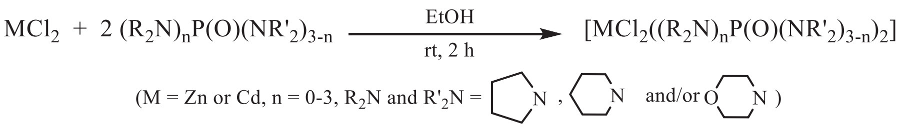
3.1. Synthesis

The variously substituted phosphoramide ligands, $R_2NP(O)(R'_2N)_2$, are new compounds and were prepared in two steps (Scheme 1). The first step is the addition of two equivalents of amine (R_2NH) to phosphoryl chloride ($POCl_3$) in diethyl ether. The second is the addition of four equivalents of the second amine (R'_2NH) to the product obtained in the first step. The resulting compounds are all colorless viscous liquids except $PyrrP(O)Mor_2$, which is a light yellow sold.

The complexes $[MCl_2L_2]$ were produced by reaction of zinc(II) or cadmium(II) chlorides in ethanol solution with the phosphoramide ligands (Scheme 2). These were purified by washing with anhydrous diethyl ether to give the pure complexes as white solids that are soluble in dichloromethane, chloroform, and nitromethane. To further confirm the adduct nature of these chloride complexes, their molar conductance in



Scheme 1. Synthesis of differently substituted phosphoramides $R_2NP(O)(NR'_2)_2$.



Scheme 2. Synthesis of zinc(II) and cadmium(II) complexes **1**–**12**.

dichloromethane (10^{-3} M) was measured and shows values in the range 1.36–11.85 $\Omega^{-1}cm^2mol^{-1}$. This indicates that these complexes are nonelectrolytes containing chloride ions with the general formula $[L_2MCl_2]$, in good agreement with our previous results obtained with other related complexes [16, 17].

3.2. Spectroscopic characterization

The complexes were characterized by IR and multinuclear (^1H, ^{13}C, and ^{31}P) NMR spectroscopy. The IR spectra (Figure 1 and Table 2) show that the stretching vibration of the P = O band is shifted to lower frequencies compared to those of free ligands, consistent with ligand P = O bond weakening upon coordination to the metal center through the oxygen of this group. This shift is more pronounced for the cadmium adducts compared to the zinc complexes. For example, the shift ($\Delta\nu_{P=O}$) for $Pyrr_3PO$ is 55 and 77 cm^{-1} in Zn complex **1** and its Cd analog **2**, respectively. Such a difference could be explained in terms of steric hindrance which would favor stronger interaction with the larger Cd ion, leading to a more lengthened PO bond. Further confirmation comes from the much higher $\Delta\nu_{P=O}$ shift value (136 cm^{-1}) observed for the still larger metal atom in the corresponding uranium(IV) complex $[UCl_4(Pyrr_3PO)_2]$ [29]. These results seem to be in agreement with those reported for similar complexes [30, 31] and with our structural study discussed below. The ^{31}P NMR spectra of the complexes were obtained at room temperature (Figure 2) and the data are listed in Table 2. The spectra show signals that are slightly shifted downfield compared to those of the free ligands, confirming the coordination of these ligands with zinc and cadmium through the P = O group. Despite the stronger donor ability of the phosphoramide ligands, the ^{31}P NMR coordination chemical shift ($\Delta^{31}P$) in **1-12** is less than 2 ppm while that of the zinc complex with a similar donor ability phosphine oxide ligand, $[ZnCl_2(n\text{-}Bu_3PO)_2]$, is much larger (14 ppm) [16]. This could be explained by the presence of a nitrogen in the former ligands, which would compensate the loss of electron density

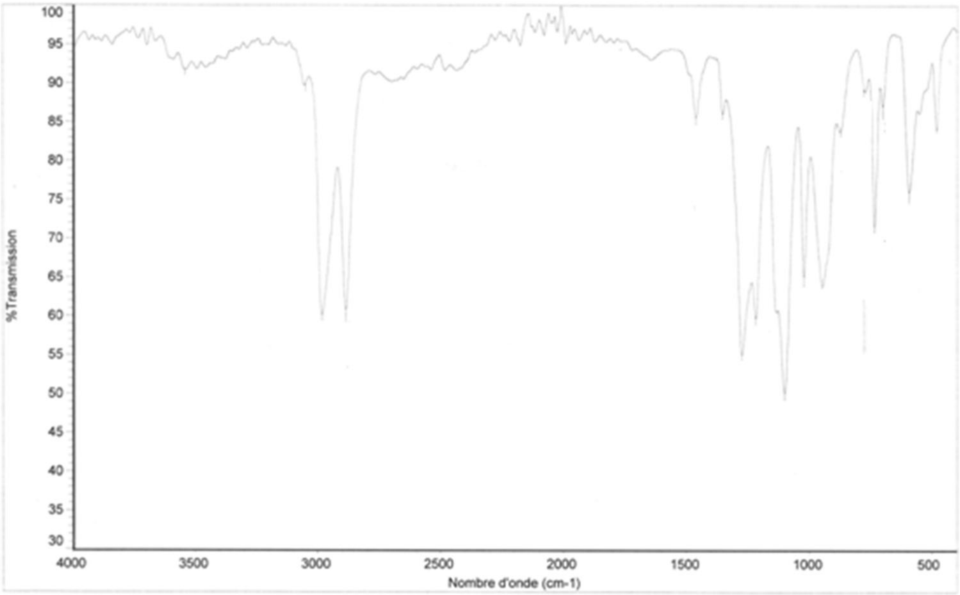


Figure 1. IR spectrum of **1** in $CHCl_3$.

Table 2. ^{31}P NMR (δ/ppm) and IR ($\nu(P=O)/cm^{-1}$) data for $[MCl_2L_2]$ (1–12).

		^{31}P ($\Delta\delta$ ^{31}P)[a]			$\nu_{P=O}$ ($\Delta\nu_{P=O}$)[b]	
Ligand (L)	L	$[ZnCl_2L_2]$	$[CdCl_2L_2]$	L	$[ZnCl_2L_2]$	$[CdCl_2L_2]$
$Pyrr_3PO$	14.20	15.72(1.52)	15.33(1.13)	1219	1161(58)	1142(77)
Pip_3PO	20.12	21.08(0.96)	21.01(0.89)	1228	1170(58)	
$MorP(O)Pyrr_2$	15.49	16.77(1.28)	16.36(0.87)	1229	1157(72)	1169(60)
$PipP(O)Pyrr_2$	16.23	17.45(1.22)	16.58(0.35)	1223	1148(75)	1143(80)
$PyrrP(O)Mor_2$	16.47	17.55(1.08)	16.93(0.46)	1212	1159(53)	1113(99)
$PyrrP(O)Pip_2$	18.44	18.53(0.09)		1232		

[a] $\Delta(\delta\ ^{31}P) = |\ \delta\ ^{31}P$ (ligand) - $\delta\ ^{31}P$ complex).
[b] $\Delta\nu(P=O) = |\nu(P=O)$(ligand) - $\nu(P=O)$(complex)$|$.

around the phosphorus upon coordination, thus resulting in a more reduced $\Delta^{31}P$. These complexes were also characterized by their ^1H NMR spectra, which display relatively broader signals that are slightly downfield shifted compared to those of free ligands.

3.3. Structural study

In order to investigate the constitution of the complexes, as well as to gain insights on the effect of the nature of the ligand donor atom on the stereochemistry and nuclearity of these complexes, we examined the solid-state structure of $[MCl_2L_2]$. Complexes **1**, **3**, **11**, and **12** gave crystals suitable for X-ray analysis. However, the other complexes were not sufficiently crystalline, even after multiple recrystallization attempts. The geometries of **1**, **3**, **11**, and **12** (Figures 3–6) are similar monomeric species, two oxygens of the two ligands and two chlorides coordinate to the metal center, giving it a distorted tetrahedral geometry. In contrast, the corresponding Zn and Cd complexes containing the sulfur or selenium donor ligands, Pip_3PS and Pip_3PSe,

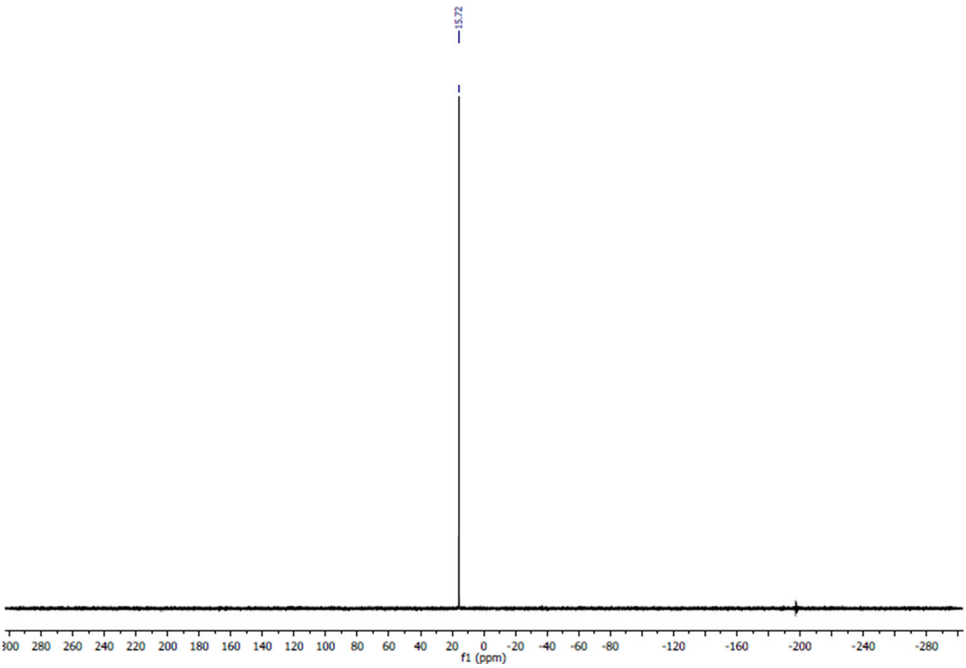


Figure 2. ^{31}P NMR spectrum of **1** in $CDCl_3$ at 25 °C.

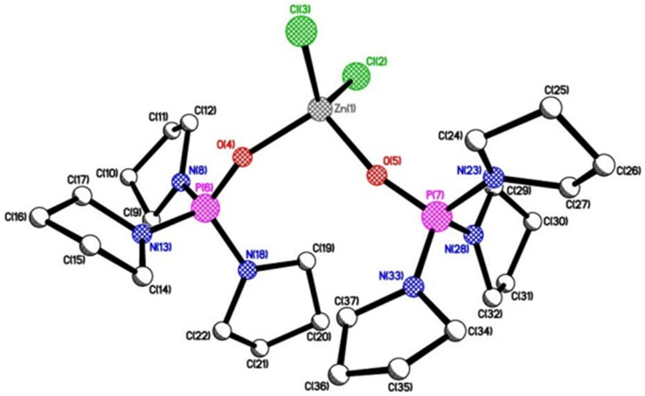


Figure 3. The X-ray crystal structure (asymmetric unit) of $[ZnCl_2(Pyrr_3PO)_2]$ (**1**). All hydrogens have been omitted for clarity.

exist as chloride bridged dimeric forms [17], showing the effect of bulkier chalcogen atoms (S and Se) on the nuclearity of such complexes. Table 3 lists important bond lengths and angles. When comparing the P = O bond distances in the zinc complex **1** (1.490(3) Å) and Cd complex **3** (1.497(4) Å), we observed that they are similar to those of corresponding Co (1.489(1) Å) [32] and Mn (1.493(2) Å) [33] complexes $[MCl_2(Pyrr_3PO)_2]$, but shorter than PO bond (1.515(7) Å) in the related uranium complex $[UCl_4(Pyrr_3PO)_2]$ [29]. The P = O bond lengths are 1.491(3), 1.484(17), 1.492(4), 1.480(4) and 1.479(5) Å for **1**, **3**, **11**, and **12**, respectively. The average P = O bond distances are all shorter than the sum of the representative covalent radii of P and O,

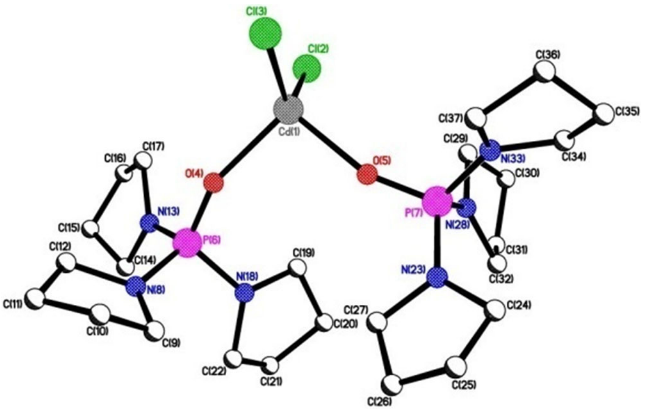


Figure 4. The X-ray crystal structure (asymmetric unit) of [$CdCl_2(Pyrr_3PO)_2$] (**3**). All hydrogens have been omitted for clarity.

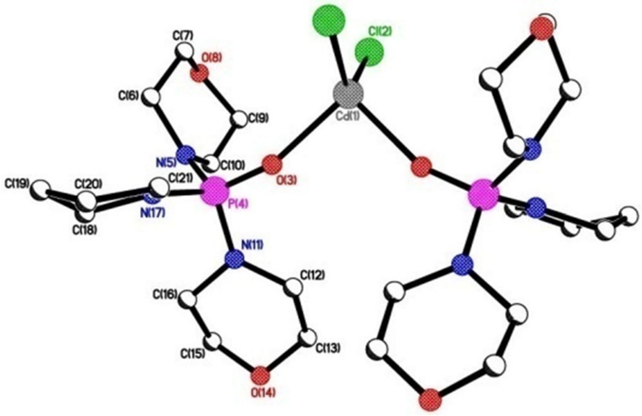


Figure 5. The X-ray crystal structure (one molecule) of [$CdCl_2(PyrrP(O)Mor_2)_2$] (**11**). All hydrogens have been omitted for clarity.

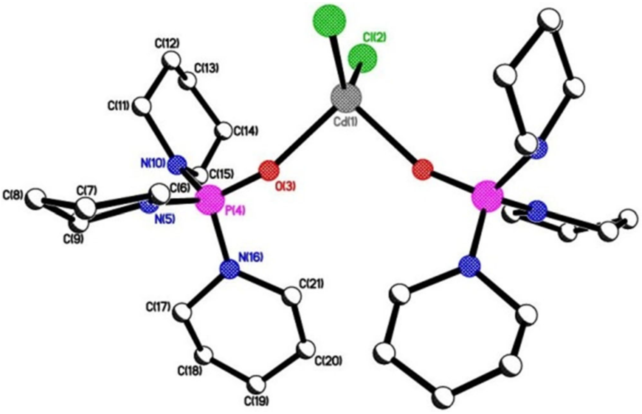


Figure 6. The X-ray crystal structure (one molecule) of [$CdCl_2(PyrrP(O)Pip_2)_2$] (**12**). All hydrogens have been omitted for clarity.

Table 3. Selected bond lengths and angles for 1, 3, 11, and 12.

	[ZnCl$_2$(Pyrr$_3$PO)$_2$] (**1**)	[CdCl$_2$(Pyrr$_3$PO)$_2$] (**3**)	[CdCl$_2$(PyrrP(O)Mor$_2$)$_2$] (**11**)	[CdCl$_2$(PyrrP(O)Pip$_2$)$_2$] (**12**)
P1-O1	1.490(3)	1.492(4)	1.480(4)	1.479(5)
P2-O2	1.489(3)	1.502(4)	1.480(4)	1.479(5)
P1-N1	1.631(3)	1.628(5)	1.636(4)	1.624(6)
P2-N2	1.625(4)	1.630(5)	1.618(4)	1.634(6)
M-Cl1	2.244(10)	2.417(14)	2.382(13)	2.386(17)
M-Cl2	2.232(10)	2.403(15)	2.382(13)	2.386(17)
M-O1	1.962(3)	2.173(4)	2.158(4)	2.156(4)
M-O2	1.953(3)	2.153(4)	2.158(4)	2.156(4)
M-O1-P1	157.17(18)	155.6(3)	156.4(3)	157.0(4)
M-O2-P2	162.4(2)	158.2(3)	156.4(3)	157.0(4)
O1-M-Cl1	107.20(8)	103.57(12)	106.99(14)	107.05(17)
O2-M-Cl2	112.20(9)	111.83(12)	112.13(15)	111.66(18)
Cl1-M-Cl2	117.51(4)	121.69(5)	121.54(9)	121.89(11)
O1-M-O2	102.45(11)	98.23(16)	93.6(3)	94.0(4)
O1-P1-N1	108.23(17)	108.4(3)	108.6(3)	108.6(3)

implying some retention of π bonding in the complex. However, these P = O distances are longer than those observed in the free ligands [34, 35]. This indicates that the P = O bond is weakened upon complex formation with the singly bonded structure becoming more pronounced with stronger donor ligands, in agreement with the order obtained from our IR and NMR data for the magnitude of metal–ligand interaction and with other related results [36]. These are also longer than the sum of covalent radii for representative single P-O bond but much shorter than the sum of van der Waals radii [37]. The structures of these complexes reveal that the average P-O-Zn angle is 157.17(18)−162.4(2)° for **1**, while that of P-O-Cd is 155.6(3)−158.2(3) for **3**, 156.4(3)° for **11** and 157.0(4) for **12**. All these angles (151.2–158.2°) are similar to those of Co (156.20(7)°) and Mn (158.9(1)°) analogs [32, 33], but much more axial than those in the corresponding S and Se analogs, which display more bent angles (less than 109°) [17]. This indicates that **1-12** could be classified as σ-donors, employing P-O σ-non-bonding electrons (lone pairs) for donation, rather than π-bonding electrons used for coordination in analogous S and Se derivatives [17], consistent with the bonding model proposed by Burford *et al.* [38]. The M–O bonds show distances of 1.930(14) to 1.962(3) Å for zinc complexes and 2.153(4) to 2.173(4) Å for the cadmium derivatives (Table 3). The average P-N distances in the complexes vary from 1.618(4) to 1.636(4) for **11**, which are shorter than in corresponding ligands [34, 36]. Finally, the M-Cl bond distances (2.169(7)−2.417(14) Å) are also shorter than the sum of corresponding covalent radii.

The degrees of tetrahedral distortion [39] in these complexes, calculated using PLATON, are 0.92, 0.89, 0.90, and 0.90 for **1**, **3**, **11**, and **12**, respectively. This suggests that the coordination around the metal center is almost a perfect tetrahedron. The pyrrolidine ligands in **1** adopt a twisted conformation, except for the N13-C17 ring which exhibits an envelope conformation on C15.

Molecular packing arrangements for **1**, **3**, **11**, and **12** are shown in Figure 7. The molecules in all four of the structures arrange themselves into sheets in the [110] plane and stack in discrete columns down the [110] and [−110] crystallographic axes. All four of the structures possess intermolecular C-H···Cl interactions: In **1**, Cl3 interacts with the adjacent molecules in two neighboring columns, along the *c* and [110]

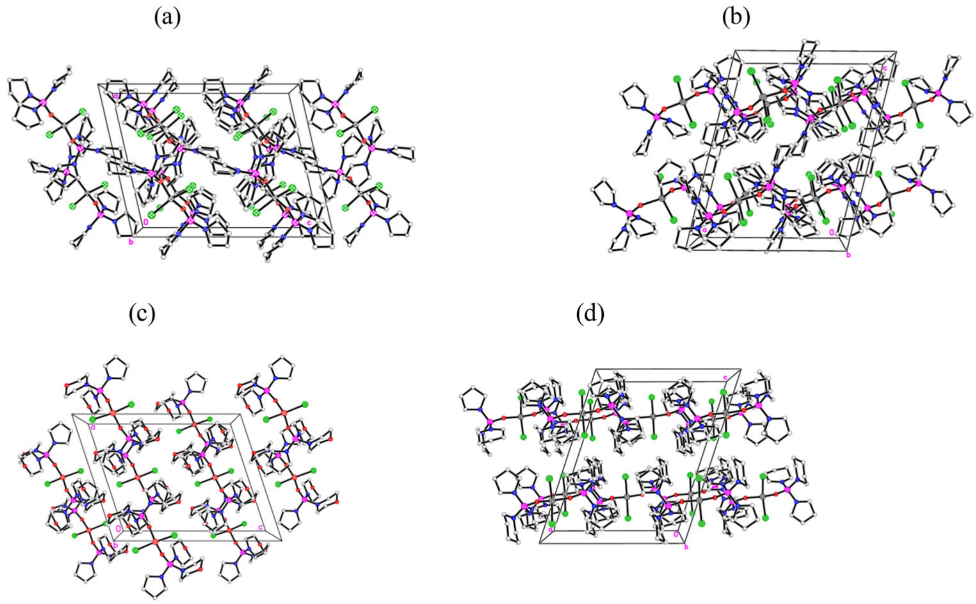


Figure 7. Molecular packing arrangements of **1** (a), **3** (b), **11** (c), and **12** (d).

directions (Figure 7(a)). In **3**, Cl2 and Cl3 both interact with the same neighboring molecule, forming zig-zagging, double C-H···Cl bonded columns down the *b*-axis. Cl3 also interacts with another neighboring molecule, an interaction which propagates down the *c*-axis (Figure 7(b)). **11** has a set of these C-H···Cl interactions propagating down the [110] and *a*-axes, along with a head to tail motif about the inversion center (Figure 7(c)). **12** shows head to tail C-H···Cl interaction which propagates down the *c*-axis. There is also a C-H···Cl interaction which propagates down the crystallographic [110] axis in **12** (Figure 7(d)).

4. Conclusion

New zinc(II) and cadmium(II) complexes with phosphoramides containing cyclic amino groups were prepared and characterized using multinuclear (^{1}H, ^{13}C, and ^{31}P) NMR, IR spectroscopy, and in some cases X-ray analysis. The X-ray data reveal that these complexes exist as monomers, in contrast to their corresponding chalcogen counterparts that form dimeric structures. In addition, the P-O-M bond angles were shown to be much more axial than those of P-E-M (E = S or Se) observed in corresponding chalcogenide analogs. This was rationalized in terms of the nature of the chalcogen donor atom involved in such complexes. The coordination chemistry of these ligands toward other metal ions is under investigation.

Disclosure statement

No potential conflict of interest was reported by the authors.

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Appendix

CCDC numbers 1951187, 1951189, 1951190 and 1951191 contains the supplementarycrystallographic data for 1, 3, 11 and 12, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.