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Specific Features of the Structure of Chelate Complexes of *N*-Thiocarbamoylamidophosphates with Zn(II) and Cd(II) Cations

F. D. Sokolov, D. A. Safin, N. G. Zabirov, P. V. Zotov, and R. A. Cherkasov

Kazan State University, Kazan, Tatarstan, Russia

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Abstract—The reaction of potassium salts of *N*-thiocarbamoylamidophosphates RC(S)NHP(O)(OPr-*i*)$_2$X [X = PhNH, *p*-MeOPhNH, *p*-BrPhNH, *i*-PrNH, *t*-BuNH, Et$_2$N, C$_5$H10N, OC$_4$H$_8$N, C$_6$H$_{11}$NH] with Zn(II) cation gives complexes of the composition Zn(L–O,S)$_2$. The Cd(II) complexes could not be isolated under analogous conditions because of their hydrolytic lability. The reaction of thioureas (X = PhNH, *p*-MeOPhNH) with Cd(II) acetate in DMF provides stable solvato complexes of the composition Cd(DMF)$_2$L$_2$. The structure of the resulting compounds was studied by means of IR, ^{1}H, and ^{31}P NMR spectroscopy and EI and ESI mass spectrometry.

N-Thioacyl- and *N*-thiocarbamoylamidophosphates of the general formula RC(S)NHP(Y)R$'_2$ (HL) (Y = O or S, R' = OAlk, OAr) **I** are organoelement analogs of β-dicarbonyl compounds [1]. They are weak NH acids (pK_a 6–9). The negative charge in their anions is distributed between the S, Y, and phosphorylamido N atoms that can be involved in complex formation [2–6].

Amidophosphates **I** have long attracted researchers's attention due to their ability to form stable chelates with IB, IIB, and VIIIB subgroup transition metal cations. These compounds and their complexes exhibit antiviral activity [7]. They can be used as stationary phases for GLC [8], as well as components of ion-selective electrodes [9-12], extractants [13], and masking reagents in analytical chemistry [2].

The interest in amidophosphates **I** is also associated with their use as structural blocks in the synthesis of supramolecular coordination compounds. The structures of *N*-thioacylamidophosphates containing crown ether substituents on the thiocarbonyl group and their complexes with Ni(II) and Cu(II) complexes has been studied [14–16]. The macroring cavities in these structures remain free and can be further involved in complex formation. Zabirov *et al.* [17, 18] have studied polynuclear complexes M$_n$L$_n$ [M = Co(II), Ni(II), Pd(II), Ag(I), Zn(II), Cd(II), Hg(II)] with bipodal amidothiophosphates of the general formula [(*i*-PrO)$_2$P(S)NHC(S)NH]$_2$Z **IIa**–**IId** [Z = (CH$_2$)$_2$O(CH$_2$)$_2$ (**IIa**), (CH$_2$)$_2$O(CH$_2$)$_2$O(CH$_2$)$_2$ (**IIb**), (CH$_2$)$_2$ (**IIc**), (CH$_2$)$_7$ (**IId**]. By means of X-ray diffraction it has been established [18] that the complex of bisamidothiophosphate **IIc** with Cd(II) cation is a macrocyclic dimer containing two Cd(II) cations a distorted tetrahedral CdS$_4$ surrounding.

By contract, coordination compounds of Zn(II) and Cd(II) cations with RC(X)NHP(Y)R$'_2$ ligands that simultaneously contain the donor atoms of sulfur and oxygen (X ≠ Y) remain practically unexplored. The appearance of the hard donor carbonyl or phosphoryl oxygen atoms in the coordination sphere of the central ion makes it coordinately unsaturated, which, in its turn, can lead to formation of heteroligand and polynuclear complexes with the central atom having the coordination number 5 or 6. Hence, amidothiophosphates **I** containing different donor atoms X and Y can have much different coordination properties compared to their dithio analogs RC(S)NHP(S)R$'_2$.

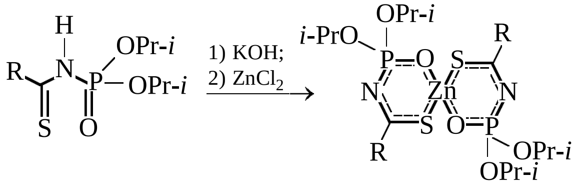
The aim of the present work was to assess the effect of the structure of amidophosphate ligands **I** (Y = O) and synthesis conditions on the composition and structure of chelate complexes of Zn(II) and Cd(II) cations. Complexes Zn[RC(S)NP(O)(OPr-*i*)$_2$–*O,S*]$_2$ were synthesized by the standard procedure [19] in the water–ethanol medium. The reaction of the potassium salts of amidophosphates **Ia**–**Ii** of the general formula RC(S)NHP(O)(OPr-*i*)$_2$ (HL) with Zn(II) cation gives complexes ZnL$_2$ (**IIIa**–**IIIi**).

Complexes **IIIa**–**IIIi** are crystalline compounds stable in air. Their IR spectra give evidence for the involvement of the C=S and P=O groups of ligands **Ia**–**Ii** in complex formation. The IR spectra of complexes **IIIa**–**IIIi** contain strong broad bands at 1512–

ESI data for the Zn(II) and Cd(II) complexes, m/z (I_{rel}, %)

Comp. no.	$[M + H]^+$	$[M + Na]^+$	$[M + K]^+$	$[2M - L]^+$	$[2M + Na]^+$
IIIa	–	717 (100)	733 (6.2)	1077 (14.9)^a	1413 (0.4)^a
IIIb	–	777 (100)	793 (5.8)	1167 (16.0)	–
IIIc	–	877 (100)^a	891 (5.6)^a	1313 (10.0)^a	–
IIId	627 (6.8)	649 (100)	665 (19.0)	975 (9.5)^a	1279 (0.6)^a
IIIe	655 (2.0)	677 (100)	693 (8.0)	1015 (21.5)^a	1334 (1.5)^a
IIIf	655 (1.6)	677 (100)	693 (10.8)	1017(1.4)^a	1335 (0.8)^a
IIIg	–	701 (100)	716 (5.2)	1049 (0.1)	–
IIIh	–	705 (100)	721 (2.5)	1056 (0.9)^a	–
IIIi	707 (11.2)	729 (100)	745 (8.4)	1093 (11.0)^a	–
IVa^b	–	767 (100)	783 (12.1)	1171 (25.5)	1511 (2.5)
IVb^b	–	827 (21.5)	842 (13.2)	1261 (5.0)	–

[a] The strongest peaks in the molecular ion cluster are presented. Unless otherwise specified, the peaks of the ions containing the most abundant isotopes are given. [b] For the marked compounds, M is the chelate nucleus of the general formula CdL_2.



Ia–**Ii** **IIIa**–**IIIi**

R = PhNH (**a**), *p*-$MeOC_6H_4NH$ (**b**), *p*-BrC_6H_4NH (**c**), *i*-PrNH (**d**), *t*-BuNH (**e**), Et_2N (**f**), $C_5H_{10}N$ (**g**), OC_4H_8N (**h**), $C_6H_{11}NH$ (**i**).

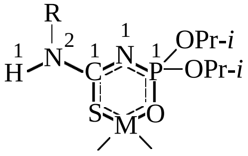
1532 and 1540–1560 cm^{-1} related to vibrations of the S$\cdots$C$\cdots$N fragment in the *N*-thioacylamidophosphate anion [19]. The P=O absorption band shifts by 76–116 cm^{-1} to low frequencies as compared to the free ligand. The IR spectra of complexes **IIIf, IIIg**, and **IIIh** lack bands characteristic of NH stretching vibrations. The IR spectra of complexes **IIIa**–**IIIe** and **IIIi** contain a single band in the range 3296–3328 cm^{-1} assignable to vibrations of the NH group of the R substituent on the thiocarbonyl carbon atom.

Complex formation causes a significant (9.5–13.4 ppm) downfield shift of the phosphorus signal of amidophosphates **Ia**–**Ii**. The ^{31}P NMR spectra of complexes **IIIa**–**IIIi** contain narrow singlet signals at δ_P 5.7–7.0 ppm.

The ^{1}H NMR spectra of chelates **IIIa**–**IIIi** contain one set of signals of the isopropoxy groups and the R substituents of the ligand anions and lack NHP(O) proton signals.

The signal of the NH proton of fragment R in chelates **IIIa**–**IIIe** and **IIIi** is shifted upfield by 3 ppm against free ligands **Ia**–**Ie** and **Ii**. This is connected with cleavage of the intramolecular hydrogen bond between the secondary NH group of the R fragment and the P=O oxygen atom in the ligands [6].

The ^{1}H NMR spectra of complexes **IIIa**–**IIIe** and **IIIi** show a signal of the NH group of the R fragment as a doublet ($^4J_{HP}$ 6.7–8.6 Hz). In the spectra of complexes **IIId** and **IIIi**, the broadened doublet of doublets of the NH group of the R fragment degenerates into a triplet ($^4J_{HP} \sim {}^3J_{HH}$). Large long-range coupling constants in Zn(II) and Cd(II) chelates with amidophosphates **I** were previously found in thiourea $PhNHC(S)NHP(S)(OPr\text{-}i)_2$ complexes [19]. The reason of the increased constant is the stability of the planar *W*-shaped conformation of the $H^1N^2C^1N^1P^1$ fragment [19].



The coupling constants in compounds **IIIa**–**IIIe** and **IIIi** depend on the nature of the R substituent and variy in the series PhNH < *p*-BrC_6H_4NH ~ *p*-$MeOC_6H_4NH$ < *i*-PrNH < *t*-BuNH. In our opinion, the reason for such an order is additional stabilization of the *W*-shaped conformation due to increased rotation barrier about the C^1–N^2 bond. In its turn, the barrier is increased by increasing steric hindrances and simultaneously increasing donor effect of the R^2 substituent, which increases the electron density on the C^1–N^2 bond.

The electron impact (EI) mass spectra of compounds **IIIa**–**IIIe** and **IIIi** contain molecular ion peaks

$[M]^+$. The relative intensities of the isotope peaks of the $[M]^+$ cluster agree with those calculated from the empirical formulas of compounds of the composition ZnL_2. Complexes **IIIa**–**IIIc** with arylamine substituents on the thiocarbonyl carbon atom have less stable molecular ions. Hence, the $[M]^+$ peak has a very low intensity (0.44%) in the mass spectrum of complex **IIIb** and absent in the mass spectra of complexes **IIIc** and **IIId**.

Investigation of complexes **IIIa**–**IIIi** by means of electrospray ionization technique (ESI) allowed to detect molecular ion peaks for all the synthesized Zn(II) complexes. The base peak in the spectrum belongs to the $[M + Na]^+$ cation (see table). The characteristic ions $[M + K]^+$ are also observed in all the spectra. The $[M + H]^+$ cations are always unstable (I_{rel} 1.6–11.2%), and for complexes **IIIa**–**IIIc, IIIg,** and **IIIh** they are not observed at all.

An interesting specific feature of the $[Zn_2L_4 + Na]^+$ compounds under discussion is the presence of weak dimer peaks and $[Zn_2L_3]^+$ fragment peaks in their ESI spectra. The complexes can dimerize by forming bridge bonds involving the donor atoms of the ligand, like in Cd(II) complexes with diphosphinylamines $R_2P(X)NHP(Y)$ [20]. In our case, the formation of dimeric structures containig tridentate bridging and bidentate terminal ligands in solution would lead to either doubling or exchange broadening of NMR signals. We failed to detect dimers of the Zn(II) complexes by spectral methods. Evidently, they are extremely unstable in solutions. However, the intensity of the $[Zn_2L_3]^+$ and $[Zn_2L_4 + Na]^+$ peaks for compounds **IIIa**–**IIIe** and **IIIi** is sufficiently high (see table), which does not completely exclude dimerization in the crystal phase.

The properties of complexes of the “soft,” easily polarizable Cd(II) cation differ considerably from those of Zn(II) chelates with the same ligands. The coordination surrounding of CdO_2S_2 occurs to be considerably less stable than of CdS_4 and ZnO_2S_2. As a result, the chelates formed are hydrolytically unstable and tend to increase the coordination number of the central atom.

Hence, attempted synthesis of Cd(II) complexes of thioureas **I** in the water–ethanol medium failed. The starting thioureas were isolated from the reaction mixture, and their unchanged structure was confirmed by EI mass spectrometry and ^1H and ^{31}P NMR spectroscopy. We suggest that the reason for the failure of the synthesis is hydrolysis of the complexes in the water–ethanol medium.

Performing the reaction of the potassium salts of thioureas **Ia** and **Ib** with $Cd(OAc)_2$ in anhydrous DMF excludes hydrolysis of the resulting chelates. But here, too, the unsaturation of the coordination surrounding of the Cd(II) cation reveals itself by the formation of stable solvato complexes $Cd(DMF)_2L_2$ (**IVa, IVb**) which were isolated from the reaction mixture and purified by repeated precipitation with hexane from methylene chloride. Their structure was studied by IR and ^1H and ^{31}P NMR spectroscopy. The composition of the complexes was confirmed by elemental analysis. Compounds **Va** and **Vb** are colorless crystalline powders stable in air.

The EI mass spectra of adducts **IVa** and **IVb** contain no molecular ion peaks. The ESI mass spectra of these complexes fragment ions characteristic of the complex nucleus CdL_2, that is $[CdL_2 + Na]^+$, $[CdL_2 + K]^+$, $[Cd_2L_3]^+$, and $[Cd_2L_4 + Na]^+$ (see table). However, the ESI spectra contain weak molecular ion peaks $[Cd(DMF)_2L_2+H]^+$ at 889(12.0) and 950(2.0) for products **IVa** and **IVb**, respectively.

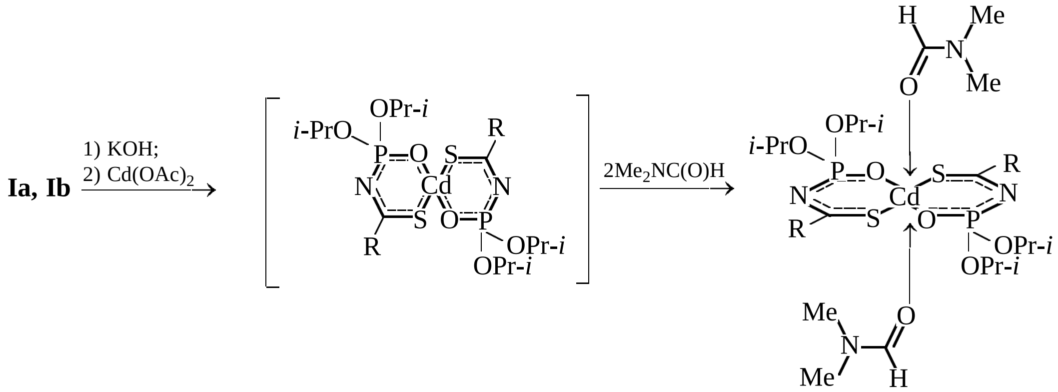
Comparative analysis of the IR spectra of thioureas **Ia** and **Ib** and their Zn(II) complexes **IIIa** and **IIIb** and adducts **IVa** and **IVb** provides evidence for the presence of a CdL_2 chelate nucleus in the latter compounds. Hence, the shift of the P=O absorption bands by 72 cm^{-1} in complexes **IVa** and **IVb** compared with free ligands **Ia** and **Ib** and the appearance of a strong absorption band of the conjugated SCN fragment confirms the 1,5-O,S coordination of the ligand anions. Along with the absorption bands typical of the anionic form of ligands **I**, the IR spectra display broad strong C=O absorption bands at 1656 cm^{-1}, related to DMF.

The phosphorus signals in the NMR spectra are located in the range characteristic of chelate complexes of ligands **I**, but they are shifted dowfield by 1–1.5 ppm aganst the signals of Zn(II) complexes of the same ligands.

The ^1H NMR spectra contain signals of the NMe_2 and C(O)H groups of coordinated DMF molecules. The $C(O)NMe_2$ protons appear as two signals of equal intensity spaced by ~20 Hz, what is connected with the nonequivalence of the DMF methyl groups due to hindered rotation about the C(O)–N bond.

The spectra show no signals of the NHP(O) groups of ligands **Ia** and **Ib**. The ratio of the integral intensities of the DMF signals and the signals of the PhNH and *i*-PrO groups of the ligands in the ^1H NMR spectra of adducts $Cd(DMF)_2L_2$ (**IVa** and **IVb**) provide further evidence for the proposed composition of the complexes.

Based on the resulting data we can suggest that complexes **IVa** and **IVb** have a tetragonal bipyramidal



IVa, IVb

R = PhNH (**a**), *p*-MeOPhNH (**b**).

structure. The axial positions in the coordination surrounding of the Cd(II) cation are occupied by the carbonyl oxygen atoms of the two DMF molecules.

We previously demonstrated the possibility of the realization of such a coordination surrounding for amidophosphates **I** containing donor atoms of different nature X and Y on an example of the complexes of the phosphorylated thiobenzamide $PhC(S)\cdot NHP(O)(OPr\text{-}i)_2$(HQ, **V**) with Co(II) [21], Ni(II) [22], and Cd(II) [23]. According to X-ray diffraction data, they have the composition $M(HQ)_2Q_2$ (**IV**). The M(II) cations have a tetragonal bipyramidal surrounding $M(O_a)_2(O_e)_2(S_e)_2$. The axial positions are occupied by two neutral molecules of ligand **V** coordinated in monodentate fashion through the P=O oxygen atoms.

Hence, our study showed that the structure and properties of Cd(II) complexes of *N*-thioacylamidophosphates $RC(S)NHP(O)R'_2$ with significantly differ from our previously studied Zn(II) complexes. The Cd(II) cation in these compounds exhibits pronounced coordination unsaturation. This results in enhanced tendency of theses complexes for hydrolysis and the ability to increase the coordination number of the central atom due to coordination with neutral donor ligands. This allows adducts of the composition $Cd(B)_2L_2$ (B = DMF, HL) to be isolated. Solvent molecules and, as we showed previously [23], neutral *N*-thioacylamidophosphate (HL) molecules can act as such ligands. Evidently, the mode of coordination of the neutral ligands in such compounds and the stability of the resulting adducts should strongly depend on the nature of the *N*-thioacylamidophosphate and the structure of the "extra" ligand. Due to that the ability of the CdL_2 complexes to react with molecules containing polar groups can further be used for design of new types of stationary phases for GLC and agents for molecular recognition and transport of organic compounds.

EXPERIMENTAL

The IR spectra IR spectra were recorded on a Specord M-80 spectrometer for suspensions in mineral oil between KBr plates in the range 400–3600 cm^{-1}. The ^{1}H (300 MHz, internal stabilization by the ^{2}H resonance line) and ^{31}P NMR spectra (121.42 MHz, external standard 85% phosphoric acid) of 0.02 M $CDCl_3$ solutions were registered on a Varian Unity 300 spectrometer (300 MHz). The EI mass spectra were obtained on TRACE MS Finnigan MAT instrument, ionizing]energy 70 eV, ion source temperature 200°C. The ampule in the direct inlet probe was heated from 35 to 150°C at 35°C/min steps. The mass spectra were treated using the Xcalibur program. The ESI mass spectra were registered on a Thermo Finnigan-LCQ instrument for 10^{-6} M solutions in $CHCl_3$–MeCN (1 : 1), sample flow rate 3 μl min^{-1}, ionizing voltage 4.10 kW, capillary temperature 210°C.

Commercially available amines vere used after repeated fractionation. Diisopropyl isothiocyanatophosphinate [24] was prepared and purified according to the published procedures. The solvents were purified and dried by conventional procedures [25]. All starting materials and solvents were freshly distilled or crystallized.

***N*-Phosphorylated thioureas Ia–Ii** *(general procedure).* A solution of 0.045 mol of amine in 15 ml of anhydrous CH_2Cl_2 was treated with vigorous stirring with a solution of 0.05 mol of diisopropoxyphosphoryl isothiocyanate in 15 ml of anhydrous CH_2Cl_2. The mixture was stirred for an additional 30 min to complete the reaction. The solvent was removed in a vacuum, and the product was purified by crystallization from a 1 : 5 mixture of methylene chloride and hexane.

***N*-(Diisopropoxyphosphoryl)-*N*'-phenylthiocarbamide (Ia)**. Colorless crystals. Yield 7.5 g (53%), mp 124–125°C (124–125°C [24]). IR spectrum, ν, $\mathrm{cm^{-1}}$: 1244 (P=O); 1012 (POC); 1508 (S–C–NH); 3136, 3304 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.20–7.26 m [1H, *p*-H(Ph)]; 7.35–7.40 m [2H, *m*-H(Ph)]; 7.60–7.62 m [2H, *o*-H(Ph)]; 1.39 d [6H, Me(*i*-PrO), $^3J_{\mathrm{HH}}$ 6.0]; 1.40 d [6H, Me(*i*-PrO), $^3J_{\mathrm{HH}}$ 6.1]; 4.75 d.septet [2H, CH(*i*-PrO), $^3J_{\mathrm{HH}}$ 6.2, $^3J_{\mathrm{PH}}$ 7.3]; 6.94 d [1H, P(O)NH, $^2J_{\mathrm{PH}}$ 6.1]; 10.78 s (1H, PhNH). ^{31}–{^{1}H} NMR spectrum : δ_{P} –5.3 ppm.

***N*-(Diisopropoxyphosphoryl)-*N*'-(*p*-methoxyphenyl)thiocarbamide (Ib)**. Light blue crystals. Yield 11.21 g (72%), mp 127–128°C. IR spectrum, ν, $\mathrm{cm^{-1}}$: 1244 (P=O); 1020 (POC); 1512 (S=C–NH); 3120, 3272 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.79 s (3H, MeO); 6.89–6.92, 7.43–7.45 m (4H, Ar); 1.38 d [12H, Me (*i*-PrO), $^3J_{\mathrm{HH}}$ 6.1]; 4.73 d.septet [2H, CH(*i*-PrO), $^3J_{\mathrm{HH}}$ 6.3, $^3J_{\mathrm{PH}}$ 7.3]; 6.67 s [1H, P(O)NH]; 10.53 s (1H, *p*-MeOPhNH). ^{31}P–{^{1}H} NMR spectrum: δ_{P} –6.9 ppm.

***N*-(Diisopropoxyphosphoryl)-*N*'-(*p*-bromophenyl)thiocarbamide (Ic)**. Pink crystals. Yield 11.38 g (64%), mp 133–134°C. IR spectrum, ν, $\mathrm{cm^{-1}}$: 1228 (P=O); 1012 (POC); 1508 (S=C–NH); 3160, 3248 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.46–7.54 m (4H, Ar); 1.37 d [6H, Me(*i*-PrO), *3J*$_{\mathrm{HH}}$ 6.1], 1.38 d [6H, Me(*i*-PrO), $^3J_{\mathrm{HH}}$ 6.0]; 4.72 d.septet [2H, CH(*i*-PrO), $^3J_{\mathrm{HH}}$ = $^3J_{\mathrm{PH}}$ 6.3]; 6.99 s [1H, P(O)NH]; 10.79 s (1H, *p*-BrPhNH). ^{31}P–{^{1}H} NMR spectrum: δ_{P} –5.8 ppm.

***N*-(Diisopropoxyphosphoryl)-*N*'-isopropylthiocarbamide (Id)**. Colorless crystals. Yield 4.1 g (32%), mp 91–92°C. IR spectrum, ν, $\mathrm{cm^{-1}}$: 1216 (P=O); 966, 1020 (POC); 1504, 1552 (S=C–NH); 3144, 3272 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.30 d [6H, Me(*i*-Pr), $^3J_{\mathrm{HH}}$ 6.5]; 4.46 d.septet [1H, CH(*i*-Pr), $^3J_{\mathrm{HH}}$ 6.6. $^3J_{\mathrm{HP}}$ 7.8]; 1.39 d [6H, Me(*i*-PrO), $^3J_{\mathrm{HH}}$ 6.1]; 1.40 d [6H, Me(*i*-PrO), $^3J_{\mathrm{HH}}$ 6.1]; 4.69 d.septet [2H, CH(*i*-PrO), $^3J_{\mathrm{HH}}$ 6.3, $^3J_{\mathrm{PH}}$ 7.5]; 7.28 d [1H, P(O)NH, $^2J_{\mathrm{PH}}$ 6.8]; 8.81 d (1H, *i*-PrNH, $^3J_{\mathrm{HH}}$ 7.8). ^{31}P–{^{1}H} NMR spectrum: δ_{P} –5.3 ppm.

***N*-(Diisopropoxyphosphoryl)-*N*'-*tert*-butylthiocarbamide (Ie)**. Colorless crystals. Yield 12.39 g (93%), mp 109–110°C (107–109°C [26]). IR spectrum, ν, $\mathrm{cm^{-1}}$: 1236 (P=O), 988, 1024 (POC); 1528 (S=C–NH); 3128, 3288 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.51 s (9H, *t*-Bu); 1.33 d [6H, Me(*i*-PrO), $^3J_{\mathrm{HH}}$ 6.0); 1.34 d [1H, P(O)NH, $^2J_{\mathrm{PH}}$ 6.0]; 4.64 d.septet [2H, CH(*i*-PrO), $^3J_{\mathrm{HH}}$ 6.2, $^3J_{\mathrm{PH}}$ 7.1], 6.34 d [1H, P(O)NH, $^2J_{\mathrm{PH}}$ 6.4], 8.87 s (1H, *t*-BuNH). ^{31}P–{^{1}H} NMR spectrum: δ_{P} –6.4 ppm.

***N*-(Diisopropoxyphosphoryl)-*N*',*N*'-diethylthiocarbamide (If)**. Colorless crystals. Yield 6.40 g (48%), mp 107–108°C. IR spectrum, ν, $\mathrm{cm^{-1}}$: 1240 (P=O); 1000, 1030 (POC); 1500, 1520 (S=C–NH); 3128 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.24 t [6H, Me(Et), $^3J_{\mathrm{HH}}$ 7.0]; 3.58–3.82 m [4H, $\mathrm{CH_2}$(Et)]; 1.36 d [6H, Me(*i*-PrO), $^3J_{\mathrm{HH}}$ 6.2]; 1.37 d [6H, Me(*i*-PrO), $^3J_{\mathrm{HH}}$ 6.1]; 4.82 d.septet [2H, CH(*i*-PrO), $^3J_{\mathrm{HH}}$ = $^3J_{\mathrm{PH}}$ 6.2]; 6.88 s [1H, P(O)NH]. ^{31}P–{^{1}H} NMR spectrum: δ_{P} –3.9 ppm.

***N*-(Diisopropoxyphosphoryl)piperidine-1-thiocarboxamide (Ig)**. Colorless crystals. Yield 12.50 g (90%), mp 67–69°C, IR spectrum, ν, $\mathrm{cm^{-1}}$: 1248 (P=O); 1000 (POC); 1506 (S=CNH); 3147 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.62–1.69 m (6H, β,γ-$\mathrm{CH_2}$, $\mathrm{C_5H_{10}N}$); 3.83–3.92 m (4H, α-$\mathrm{CH_2}$, $\mathrm{C_5H_{1)}N}$); 1.36 d [12H, Me(*i*-PrO), $^3J_{\mathrm{HH}}$ 6.2]; 4.77 d.septet [2H, CH(*i*-PrO), $^3J_{\mathrm{HH}}$ 6.3, $^3J_{\mathrm{PH}}$ 7.3]; 7.65 s [1H, P(O)NH]. ^{31}P–{^{1}H} NMR spectrum: δ_{P} –3.4 ppm.

***N*-(Diisopropoxyphosphoryl)morpholine-4-thiocarboxamide (Ih)**. Colorless crystals. Yield 13.40 g (96%), mp 99–101°C. IR spectrum, ν, $\mathrm{cm^{-1}}$: 1236 (P=O); 1020 (POC); 1508 (S=C–NH); 3128 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.69–3.72 m [4H, ($\mathrm{OC_4H_8N}$)]; 3.94–3.97 m [4H, ($\mathrm{OC_4H_8N}$)]; 1.33 d [12H, Me(*i*-PrO), $^3J_{\mathrm{HH}}$ 6.1]; 4.73 d.sept [2H, CH(*i*-PrO), $^3J_{\mathrm{HH}}$ 6.3, $^3J_{\mathrm{PH}}$ 7.2]; 8.26 s [1H, P(O)NH]. ^{31}P–{^{1}H} NMR spectrum: δ_{P} –3.8 ppm.

***N*-Cyclohexyl-*N*'-(diisopropoxyphosphoryl)thiocarbamide (If)**. Colorless crystals. Yield 15.78 g (98%), mp 108–110°C (107.5–109 [26]). IR spectrum, ν, $\mathrm{cm^{-1}}$: 1220 (P=O), 1016 (POC); 1500, 1552 (S=C–NH); 3160, 3280 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.08–1.48 m (5H, multiplet overlapping with *i*-PrO methyl proton signals), 1.48–1.76 m (3H), 1.88–2.08 m (2H), [β,γ,δ-$\mathrm{CH_2}$ ($\mathrm{C_6H_{11}N}$)], 4.08–4.22 m [1H, CHN ($\mathrm{C_6H_{11}N}$)]; 1.33 d [6H, Me(*i*-PrO), $^3J_{\mathrm{HH}}$ 6.2]; 1.34 d [6H, Me(*i*-PrO), $^3J_{\mathrm{HH}}$ 6.1)]; 4.63 d.septet [2H, CH(*i*-PrO), $^3J_{\mathrm{HH}}$ 6.3, $^3J_{\mathrm{PH}}$ 7.4]; 6.84 d [1H, P(O)NH, $^2J_{\mathrm{PNH}}$ 4.5]; 8.83 d (1H, $\mathrm{C_6H_{11}}\cdot$NH, $^3J_{\mathrm{HCNH}}$ 7.4). ^{31}P–{^{1}H} NMR spectrum: δ_{P} –4.8 ppm.

Zn(II) complexes IIIa–IIIi) *(general procedure).* A solution of 0.005 mol of compound **Ia**–**Ii** in 10 ml of ethanol was treated with a solution of 0.0055 mol (10%) of KOH in 20 ml of ethanol. The reaction mixture was stirred for 30 min, and then a solution of 0.0075 mol (50% excess) of $\mathrm{ZnCl_2}$ in 20 ml of distilled water was added dropwise. After the addition was complete, the reaction mixture was stirred for 3–4 h. The product was extracted from the reaction mixture with small portions of CH_2Cl_2, and the combined solutions were dried over $MgSO_4$. The solvent was removed, and the product was crystallized from a 1:5 methylene chloride–hexane mixture. The resulting complexes all were colorless crystals.

Bis[*N*-(diisopropoxyphosphoryl)-*N*'-phenylthiocarbamido-*O,S*]zinc(II) (IIIa). Yield 0.99 g (57%), mp 118–119°C. IR spectrum, ν, cm^{-1}: 1096, 1140 (P=O); 1000 (POC); 1528, 1560 ($S\overset{\cdots}{-}C\overset{\cdots}{-}N$); 3312 (NH). ^1H NMR spectrum, δ, ppm (*J*, Hz): 4.05–7.10 m [2H, *p*-H(Ph)]; 7.25–7.30 m [4H, *m*-H(Ph)]; 7.48–7.50 m [4H, *o*-H(Ph)]; 1.31 d [24H, Me(*i*-PrO), $^3J_{HH}$ 6.3]; 4.63 d.septet [4H, CH(*i*-PrO), $^3J_{HH}$ 6.2, $^3J_{PH}$ 7.6]; 7.57 d (2H, PhNH, $^4J_{HNCNP}$ 6.7). $^{31}P–\{^1H\}$ NMR spectrum: δ_P 6.3 ppm. Mass spectrum, *m/z* (I_{rel}, %): 694.40 $[M]^+$ (0.4), 661 $[M – SH]^+$ (0.6), 602 $[M – PhNH]^+$ (1.1), 316 [HL] (60.6), 282 (69.8), 274 (15.8), 240 (58.2), 198 (100), 181 (50.3), 152 (39.5), 135 (46.7), 118 (98.2), 93 (79.4), 77 (49.0), 65 (54.9), 43 $[C_3H_7]^+$ (78.0). Found, %: C 44.83, H 5.74, N 8.07, P 8.93, S 9.19, Zn 9.37. $C_{26}H_{40}N_4O_6P_2S_2Zn$. Calculated, %: C 44.86, H 5.79, N 8.05, P 8.90, S 9.21, Zn 9.39.

Bis[*N*-(diisopropoxyphosphoryl)-*N*'-(*p*-methoxyphenyl)thiocarbamido-*O,S*]zinc(II) (IIIb). Yield 1.39 g (74%), mp 116–117°C. IR spectrum, ν, cm^{-1}: 1104, 1136 (P=O); 1020 (POC); 1512 ($S\overset{\cdots}{-}C\overset{\cdots}{-}N$); 3296 (NH). ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.76 s (6H, MeO); 6.79–6.82, 7.35–7.39 m (8H, Ar); 1.26 d [24H, Me(*i*-PrO), $^3J_{HH}$ 6.2]; 4.57 d.septet [4H, CH(*i*-PrO), $^3J_{HH}$ = $^3J_{PH}$ 6.1]; 7.47 d (2H, *p*-MeOPhNH, $^4J_{HNCNP}$ 7.7). $^{31}P–\{^1H\}$ NMR spectrum: δ_P 6.5 ppm. Mass spectrum, *m/z* (I_{rel}, %) $[M]^+$ absent. Found, %: C 44.46, H 5.88, N 7.44, P 8.22, S 8.50, Zn 8.42. $C_{28}H_{44}N_4O_8P_2S_2Zn$. Calculated, %: C 44.48, H 5.87, N 7.41, P 8.19, S 8.48, Zn 8.65.

Bis[*N*-(*p*-bromophenyl)-*N*'-(diisopropoxyphosphoryl)thiocarbamido-*O,S*]zinc(II) (IIIc). Yield 2.04 g (96%), mp 178–179°C. IR spectrum, ν, cm^{-1}: 1100, 1128 (P=O); 1028 (POC); 1516, 1560 ($S\overset{\cdots}{-}C\overset{\cdots}{-}N$); 3304 (NH). ^1H NMR spectrum, δ, ppm (*J*, Hz): 7.37 s (8H, Ar); 1.29 d [24H, Me(*i*-PrO), $^3J_{HH}$ 6.0]; 4.59 d.sept [4H, CH(*i*-PrO), $^3J_{HH}$ 6.2, $^3J_{PH}$ 7.0]; 7.53 d (2H, *p*-BrPhNH, $^4J_{HNCNP}$ 7.7). $^{31}P–\{^1H\}$ NMR spectrum: δ_P 6.2 ppm. Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ absent. Found, %: C 36.60, H 4.46, Br 18.70, N 6.55, P 7.28, S 7.53, Zn 7.70. $C_{26}H_{38}Br_2M_4O_6 \cdot P_2S_2Zn$. Calculated, %: C 36.57, H 4.49, Br 18.72, N 6.56, P 7.25, S 7.51, Zn 7.66.

Bis[*N*-(diisopropoxyphosphoryl)-*N*'-isopropylthiocarbamido-*O,S*]zinc(II) (IIId). Yield 1.57 g (68%), mp 124–125°C. IR spectrum, ν, cm^{-1}: 1104, 1140 (P=O); 1008 (POC); 1532 ($S\overset{\cdots}{-}C\overset{\cdots}{-}N$); 3312 (NH). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.10 d [12H, Me(*i*-Pr), $^3J_{HH}$ 6.5]; 4.07 d.septet [2H, CH(*i*-Pr), $^3J_{HH}$ 6.8, $^3J_{HNNNH}$ 7.1]; 1.27 d [12H, Me(*i*-PrO), $^3J_{HH}$ 6.1]; 1.28 d [12H, Me(*i*-PrO), $^3J_{HH}$ 6.1]; 4.57 d.septet [4H, CH(*i*-PrO), $^3J_{HH}$ 6.5, $^3J_{PN}$ 7.0]; 5.70 t (2H, *i*-PrNH, $^2J_{HNCNP}$ = $^3J_{HH}$ 8.0). $^{31}P–\{^1H\}$ NMR spectrum: δ_P 7.0 ppm. Mass spectrum, *m/z* (I_{rel}, %): 626 $[M]^+$ (18.4), 563 $[M – SH]^+$ (1.15), 584 $[M – C_3H_6]^+$ (1.54), 568 $[M – i\text{-}PrNH]^+$ (3.6), 536 (3.9), 510 (8.4), 468 (5.6), 402 (8.5), 346 (12.2), 282 [HL] (37.3), 265 (14.6), 261 (14.3), 240 (11.6), 197 (27.1), 165 (80.3), 123 (100.0), 98 (43.3), 83 (66.0), 58 (88.4), 43 $[C_3H_7]^+$ (92.5). Found, %: C 38.27, H 7.03, N 8.89, P 9.90, S 10.23, Zn 10.22. $C_{20}H_{44}N_4O_6P_2S_2Zn$. Calculated, %: C 38.25, H 7.06, N 8.92, P 9.86, S 10.21, Zn 10.41.

Bis[*N*-*tert*-butyl-*N*'-(diisopropoxyphosphoryl)thiocarbamido-*O,S*]zinc(II) ((IIIe). Yield 1.61 g (95%), mp 166–167°C. IR spectrum, ν, cm^{-1}: 1108, 1144 (P=O); 1004, 1032 (POC); 1516, 1544 ($S\overset{\cdots}{-}C\overset{\cdots}{-}N$); 3328 (NH). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.32 s (18H, *t*-Bu); 1.26 d [12H, Me(*i*-PrO), $^3J_{HH}$ 6.4]; 1.29 d [12H, Me(*i*-PrO), $^3J_{HH}$ 6.5]; 4.57 d.septet [4H, CH(*i*-PrO), $^3J_{HH}$=$^3J_{PH}$ 6.4]; 4.78 d (2H, *t*-BuNH, $^4J_{HNCNP}$ 8.6). $^{31}P–\{^1H\}$ NMR spectrum: δ_P 5.7 ppm. Mass spectrum, *m/z* (I_{rel}, %): 654 $[M]^+$ (14.0), 621 $[M – SH]^+$ (3.4), 598 $[M – C_4H_6]^+$ (19.0), 565 $[M – C_4H_6–SH]^+$ (6.4), 542 $[M – 2C_4H_6]^+$ (30.0), 523 (8.3), 509 (6.8), 500 (11.6), 481(8.5), 467 (8.6), 458 (8.6), 425 (8.6), 341 (11.4), 306 (18.0), 295 $[M – ZnL]^+$ (49.1), 296 (45.9), 265 (25.1), 253 (41.6), 211 (58.0), 165 (76.5), 156 (68.3), 123 (100.0), 97 $[ZnSH]^+$ (39.3), 83 (54.6), 57 $[t\text{-}Bu]^+$ (55.2), 43 $[C_3H_7]$ (56.6). Found, %: C 40.31, H 7.34, N 8.55, P 9.41, S 9.81, Zn 9.99. $C_{22}H_{48}N_4O_6P_2S_2Zn$. Calculated, %: C 40.28, H 7.37, N 8.54, P 9.44, S 9.77, Zn 9.97.

Bis[*N,N*-diethyl-*N*'-(diisopropoxyphosphoryl)thiocarbamido-*O,S*]zinc(II) (IIIf). Yield 1.50 g (92%), mp 58–59°C. IR spectrum, ν, cm^{-1}: 1104, 1135 (P=O); 996 (POC); 1520 ($S\overset{\cdots}{-}C\overset{\cdots}{-}N$). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.06 t [6H, Me(Et), $^3J_{HH}$ 7.0]; 1.17 t [6H, Me(Et), $^3J_{HH}$ 7.0]; 3.48 q [4H, CH_2(Et), $^3J_{HH}$ 6.9]; 3.71 q [4H, CH_2(Et), $^3J_{HH}$ 6.6]; 1.24 d [24H, Me(*i*-PrO), $^3J_{HH}$ 6.1]; 4.54 d.septet [4H, CH(*i*-PrO), $^3J_{HH}$ = $^3J_{PH}$ 6.3]. $^{31}P–\{^1H\}$ NMR spectrum: δ_P 5.6 ppm. Mass spectrum, *m/z* (I_{rel}, %): 654 $[M]^+$ (40.8), 625 $[M – Et]^+$ (5.0), 582 $[M – Et_2N]^+$ (32.1), 556 (4.8), 540 (10.7), 524 (12.2), 498 (16.8), 482 (12.4), 456 (18.4), 414 (36.7), 380 (20.1), 360 (25.5), 355 (20.9), 275 (40.8), 227 (21.3), 179 (100.0), 151 (30.0), 123 (18.4), 99 (40.0), 72 $[Et_2N]^+$ (77.8), 43 $[C_3H_7]^+$ (59.3). Found, %: C 20.31, H 7.40, N 8.52, P 9.41, S 9.81, Zn 9.95. $C_{22}N_{48}N_4O_6P_2S_2Zn$.

Calculated, %: C 40.28, H 7.37, N 8.54, P 9.44, S 9.77, Zn 9.97.

Bis[*N*-(diisopropoxyphosphoryl)piperidine-1-thiocarboxamido-*O,S*]zinc(II) (IIIg). Yield 1.41 g (83%), mp 74–75°C. IR spectrum, ν, cm^{-1}: 1104, 1144 (P=O); 996 (POC); 1504 ($S\overset{\cdots}{-}C\overset{\cdots}{-}N$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.46 br.s [4H, γ-CH$_2$, (C$_5$H$_{10}$N)]; 1.57 br.s [8H, β-CH$_2$, (C$_5$H$_{10}$N)]; 3.74 br.s [4H, α-CH$_2$, (C$_5$H$_{1)}$N)], 3.96 br.s [4H, α-CH$_2$, (C$_5$H$_{10}$N)]; 1.25 d [24H, Me(*i*-PrO), $^3J_{HH}$ 6.4]; 4.54 d.septet [4H, CH(*i*-PrO), $^3J_{HH}$ = $^3J_{PH}$ 6.4]. ^{31}P–{^{1}H} NMR spectrum: δ$_P$ 6.1 ppm. Mass spectrum, *m/z* (I_{rel}, %): 678 [*M*]$^+$ (19.4), 594 [*M* – C$_5$H$_{10}$N]$^+$ (10.43), 568 (4.58), 552 (3.98), 536 (8.52), 510 (6.2), 468 (6.9), 454 (9.3), 426 (17.1), 372 (17.2), 333 (11.2), 287 (22.0), 269 (8.5), 239 (11.9), 207 (14.8), 191 (36.1), 166 (8.4), 140 (20.7), 123 (16.5), 111 (28.6), 84 [C$_5$H$_{10}$N]$^+$ (100.0), 43 [C$_3$H$_7$]$^+$ (40.5). Found, %: C 42.35, H 7.13, N 8.22, P 9.13, S 9.44, Zn 9.62. $C_{24}H_{48}N_4O_6P_2S_2Zn$. Calculated, %: C 42.38, H 7.11, N 8.24, P 9.11, S 9.43, Zn 9.61.

Bis[*N*-(diisopropoxyphosphoryl)morpholine-4-thiocarboxamido-*O,S*]zinc(II) (IIIh). Yield 1.35 g (79%), mp 70–71°C. IR spectrum, cm^{-1} (*J*, Hz): 3.62 br.s [4H, OCH$_2$ (OC$_4$H$_8$N)]; 3.66 br.s [4H, OCH$_2$(OC$_4$H$_8$N)]; 3.81 br.s [4H, NCH$_2$ (OC$_4$H$_8$N)]; 4.03 br.s [4H, NCH$_2$(OC$_4$H$_8$N)]; 1.27 d [24H, Me(*i*-PrO), $^3J_{HH}$ 6.2]; 4.55 d.septet [4H, CH(*i*-PrO), $^3J_{HH}$ 6.4, $^3J_{PH}$ 7.5]. ^{31}P–{^{1}H} NMR spectrum: δ$_P$ 6.4 ppm. Mass spectrum, *m/z* (I_{rel}, %): 6.82 [*M*]$^+$ (33.8), 619 (7.9), 596 [*M* – C$_4$H$_8$NO]$^+$ (27.5), 570 (2.9), 554 (9.8), 538 (9.9), 512 (14.0), 470 (22.4), 428 (57.3), 369 (30.4), 335 (22.7), 321 (16.5), 289 (50.1), 209 (28.4), 193 (67.3), 166 (18.5), 140 (43.4), 123 920.8), 113 (61.2), 86 (70.2), 57 (54.8), 43 [C$_3$H$_7$]$^+$ (100). Found, %: C 38.65, H 6.51, N 8.17, P 9.09, S 9.34, Zn 9.53. $C_{22}H_{44}N_4O_8P_2S_2Zn$. Calculated, %: C 38.63, H 6.48, N 8.19, P 9.06, S 9.37, Zn 9.56.

Bis[*N*-cyclohexyl-*N*'-(diisopropoxyphosphoryl)-thiocarbamido-*O,S*]zinc(II) (IIIi). Yield 1.11 g (63%), mp 110–111°C. IR spectrum, ν, cm^{-1}: 1104, 1132 (P=O); 1016 (POC); 1532 ($S\overset{\cdots}{-}C\overset{\cdots}{-}N$); 3312 (NM). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.05–1.17 m (6H, multiplete overlapping with *i*-PrO methyl proton signals), 1.50–1.66 m (6H), 1.84–2.01 m (8H), [β,γ,δ-CH$_2$(C$_6$H$_{11}$N)]; 3.66–3.82 m (2H, CHN(C$_6$H$_{11}$N)]; 1.25 d [12H, Me(*i*-PrO), $^3J_{HH}$ 6.1]; 1.26 d [12H, Me(*i*-PrO), $^3J_{HH}$ 6.0]; 4.53 m [4H, CH(*i*-PrO), $^3J_{HH}$ 6.4, $^3J_{PH}$ 6.3]; 5.74 t (2H, C$_6$H$_{11}$N*H*, $^4J_{HNCNP}$ = $^3J_{HH}$ 7.3). ^{31}P–{^{1}H} NMR spectrum: δ$_P$ 7.1 ppm. Mass spectrum, *m/z* (I_{rel}, %): 706 [*M*]$^+$ (2,5), 673 [*M* – CH]$^+$ (0.4), 6.24 [*M* – C$_6$H$_{10}$]$^+$ (0.9), 608 [*M* – C$_6$H$_{11}$NH]$^+$ (0.6), 322 (44.0), 279 (18.3), 247 (14.5), 237 (41.6), 205 (79.0), 165 (22.5), 157 (76.5), 123 (100.0), 98 (94.9), 81 (63.4), 55 (71.3), 43 [C$_3$H$_7$]$^+$ (92.5). Found, %: C 44.07, H 7,38, N 7.93, P 8.74, S 9.08, Zn 9.26. $C_{26}H_{52}N_4O_6P_2S_2Zn$. Calculated, %: C 44.07, H 7.38, N 7.93, P 8.74, S 9.08, Zn 9.26. $C_{26}H_{52}N_4O_6P_2S_2Zn$. Calculated, %: C 44.10. H 7.40, N 7.91, P 8.75, S 9.05, Zn 9.23.

Cd(DMF)$_2$L$_2$ complexes IVa and IVb *(general procedure)*. A solution of 0.0045 mol of compound **Ia** or **Ib** in 20 ml of acetone was treated with a solution of 0.009 mol (100% excess) of KOH, and 0.1 g of 18-crown-6 was added. The reaction mixture was stirred for 1 h, and a solution of 0.0023 mol of Cd(AcO)$_2$ 2H$_2$O in 5 ml of DMF was added dropwise with stirring. After the addition was complete the reaction mixture was stirred for an additional 1 h. The resulting solution was filtered off, the solvent was removed, and the residue was crystallized from a 1 : 5 mixture of methylene chloride and hexane. The complexes were obtained as fine crystalline colorless powders.

Bis[*N*-(diisopropoxyphosphoryl)-*N*'-phenylthiocarbamido-*O,S*]bis(dimethylformamide-*O*)-cadmium(II) (IVa). Yield 0.46 g (27%), mp 126–127°C. IR spectrum, ν, cm^{-1}: 1172 (P=O); 1012 (POC); 1536 ($S\overset{\cdots}{-}C\overset{\cdots}{-}N$); 3232 (NH), 1656 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.92–6.96 m [2H, H$_p$ (Ph)]; 7.14–7.19 m [4H, H$_m$ (Ph)]; 7.52–7.54 m [4H, H$_o$ (Ph)]; 1.21 d [12H, Me(*i*-PrO), $^3J_{HH}$ 6.1]; 1.24 d [12H, Me(*i*-PrO), $^3J_{HH}$ 6.2]; 4.52 d.septet [4H, CH(*i*-PrO), $^3J_{HH}$ = $^3J_{PH}$ 6.4]; 8.21 s (2H, PhNH), 2.87 s [6H, Me(DMF)]; 2.94 s [6H, Me(DMF)]; 8.00 s [2H, C(O)H(DMF)]. ^{31}P–{^{1}H}: δ 7.5 ppm. Mass spectrum, *m/z* (I_{rel}, %): [*M*]$^+$ absent. Found, %: C 43.25, H 6.14, Cd 12.61, N 9.48, P 6.99, S 7.22. $C_{32}H_{54}CdN_6O_8P_2S_2$. Calculated, %: C 43.22, H 6.12, Cd 12.64, N 9.45, P 6.97, S 7.21.

Bis[*N*-(diisopropoxyphosphoryl)-*N*'-(*p*-methoxyphenyl)thiocarbamido-*O,S*]bis(dimethylformamide-*O*)cadmium(II) (IVb). Yield 0.89 g (48%), mp 122–124°C. IR spectrum, ν, cm^{-1}: 1172 (P=O); 1010 (POC); 1538 ($S\overset{\cdots}{-}C\overset{\cdots}{-}N$); 3235 (NH), 1660 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.73 s [6H, Me(MeO)]; 6.72–6.75, 7.37–7.40 m (8H, Ar); 1.18 d [12H, Me(*i*-PrO), $^3J_{HH}$ 5.8]; 1.24 d [12H, Me(*i*-PrO), $^3J_{HH}$ 5.9]; 4.47 d.septet [4H, CH(*i*-PrO), $^3J_{HH}$ = $^3J_{PH}$ 6.1]; 7.86 s (2H, *p*-MeOPhNH); 2.85 s [6H, Me(DMF)]; 2.92 s [6H, Me(DMF)]; 7.99 s [2H, C(O)H(DMF)]. ^{31}P–{^{1}H} NMR spectrum: δ$_P$ 7.9 ppm. Mass spectrum, *m/z* (I_{rel}, %): [*M*]$^+$ absent. Found, %: C 42.99, H 6.13, Cd 11.85, N 8.87, P 6.56, S 6.73. $C_{34}H_{58}CdN_6O_{10}P_2S_2$. Calculated, %: C 43.02, H 6.16, Cd 11.84, N 8.85, P 6.53, S 6.75.

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