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Coordination Mode of the Zinc(II) and Cadmium(II) Cations with *N*-(Diisopropoxyphosphoryl)thiobenzamide

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Reaction of the potassium salt of *N*-(diisopropoxyphosphoryl)thiobenzamide ($(i\text{PrO})_2\text{P(O)NHC(S)C}_6\text{H}_5$ (**HL**) with Zn^{II} and Cd^{II} cations in aqueous EtOH leads to three different complexes: [Zn(L-*O*,*S*)$_2$] (**1**), [Cd$_2$(L-*O*,*S*)$_4$] (**2**) and [Cd(HL-*O*)$_2$(L-*O*,*S*)$_2$] (**3**). The structures of these compounds were investigated by single-crystal X-ray diffraction analysis, EI-MS and ES-MS, IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and microanalysis. The zinc(II) atom in complex **1** is in a distorted tetrahedral ZnO_2S_2 environment formed by the C=S sulfur atoms and the P=O oxygen atoms of two deprotonated ligands. The cadmium(II) complex **2** is centrosymmetric and consists of dimeric species. Two [Cd(L-*O*,*S*)$_2$] moieties are connected by two bridging [S–Cd–S] units through the sulfur atoms of the ligand C=S groups. Complex **2** has a distorted trigonal-bipyramidal $\text{Cd(O}^{\text{ax}})_2(\text{S}^{\text{eq}})_3$ core. Complex **3** has a tetragonal-bipyramidal environment, $\text{Cd(O}^{\text{ax}})_2(\text{O}^{\text{eq}})_2(\text{S}^{\text{eq}})_2$, and two neutral ligand molecules are coordinated in the axial positions through the oxygen atoms of the P=O groups. The base of the bipyramid is formed by two anionic ligands in a typical 1,5-O,S coordination mode. The ligands are in a *trans* configuration.

Introduction

Amidophosphates of the type RC(X)NHP(Y)R′$_2$ (X, Y = O or S; R = Alk, Ar, ArNH, AlkNH, Alk$_2$N; R′ = OAlk, OAr, Ar) are attractive because of their ability to form stable chelates with d- and f-metal cations. These complexes possess antivirus[1] and anticancer activity,[2] and show nonlinear optical properties.[3] They can be used as components of ion-selective electrodes,[4–7] or as extragents and masking reagents in analytical chemistry.[8,9]

An application as structural blocks for the synthesis of supramolecular coordination compounds has excited a new wave of interest in the coordination chemistry of amidophosphates[10,11] and their nearest analogues such as 1,3-dichalcogenimidodiphosphinates R$_2$P(X)NHP(Y)R′$_2$[12] or carbamoylphosphane oxide R$_2$P(O)CH$_2$C(X)R′.[13] Polynuclear complexes of the type M_nL_n (M = Co^{II}, Ni^{II}, Pd^{II}, Ag^{I}, Zn^{II}, Cd^{II}, Hg^{II}) of bis(bipodal) amidothiophosphates with the general formula $[(i\text{PrO})_2\text{P(S)NHC(S)NH}]_2\text{Z}$ [Z = $(\text{CH}_2)_2\text{O}(\text{CH}_2)_2$, $(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2$, $(\text{CH}_2)_2$, $(\text{CH}_2)_7$] have been investigated.[14,15] It was established that the cadmium(II) complex with bipodal amidophosphate, where Z = $(\text{CH}_2)_2$,[15] represents a macrocyclic dimer (n = 2) containing two Cd^{II} cations in a distorted tetrahedral CdS_4 environment.

The structure of Zn^{II} and Cd^{II} complexes with the general formula M[L-*S*,*S*′]$_2$ {L = $[\text{H}_2\text{NC(S)NP(S)(C}_6\text{H}_5)_2]^-$, M = Zn^{II};[16] L = $[\text{C}_6\text{H}_5\text{NHC(S)NP(S)(O}i\text{Pr)}_2]^-$, M = Zn^{II} or Cd^{II};[17] L = $[\text{C}_6\text{H}_5\text{C(S)NP(S)(O}i\text{Pr)}_2]^-$, M = Zn^{II}[17] and Cd^{II}[18]} has been investigated by IR and NMR spectroscopy[16–18] and X-ray analysis.[16] It was established that, in all cases, there is chelate formation in which the metal cation has a distorted tetrahedral MS_4 environment.

In contrast to dithio derivatives, the Zn^{II} and Cd^{II} complexes with *N*-acylamidophosphates RC(X)NHP(Y)R′$_2$, containing both donor atoms of sulfur and oxygen (X $\neq$ Y), were not studied earlier. The substitution of two sulfur atoms in the central ion coordination sphere by oxygen atoms lowers the degree of stabilisation of π interactions. This leads to an increase in the coordination numbers of the Zn^{II} and Cd^{II} cation from 4 to 5 and 6, respectively. For example, it is known that Cd^{II} complexes with R$_2$P(X)NHP(Y)R′$_2$ (X = S, Y = O or X = Y = O) exhibit dinuclear structures in which the imidodiphosphinate anions act simultaneously as didentate ligands and as bridging units through the oxygen atoms of the P=O groups.[12]

The present work was carried out with the aim of appraising the influence of the cation (M^{II} = Zn^{II} and Cd^{II}) on the formation of either mono- or dinuclear complexes with the amidophosphate ligand $(i\text{PrO})_2\text{P(O)NHC(S)C}_6\text{H}_5$ (**HL**).

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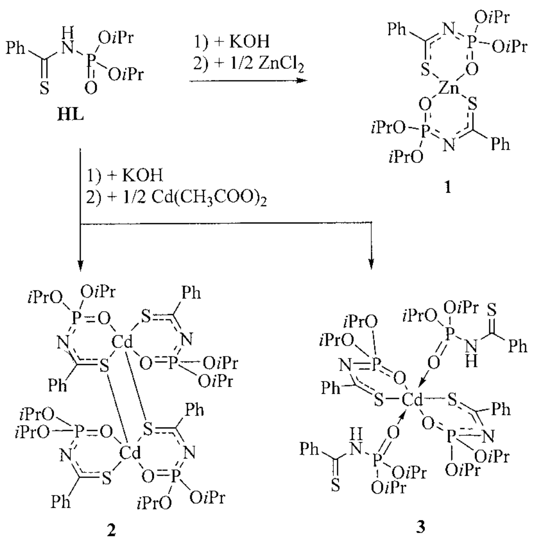
Results and Discussion

Synthesis

The ligand **HL** was prepared by reaction of thiobenzamide $C_6H_5C(S)NH_2$ with diisopropyl chlorophosphate $(i\text{PrO})_2P(O)Cl$.

Complexes of **HL** with Zn^{II} and Cd^{II} cations (**1**–**3**) were prepared by the following procedure: the ligand was converted into the potassium salt **KL**, followed by reaction with salts of the corresponding metals. The compounds obtained are crystalline solids that are soluble in most polar solvents. Reaction of the salt **KL** with $ZnCl_2$ in aqueous EtOH leads only to the formation of the complex $[ZnL_2]$ (**1**). Reaction with $Cd(CH_3COO)_2$ leads to the formation of two complexes: $[Cd_2L_4]$ (**2**) and $[Cd(HL)_2L_2]$ (**3**) (Scheme 1). Complex **3** was separated from the mixture by extraction with *n*-hexane.



Scheme 1.

It has been shown that in the crystal form all listed complexes have various coordination environments at the metal atoms. The IR and NMR spectroscopic data confirm that in $CDCl_3$ and CCl_4 solutions and in all three cases the dominating forms are $[ML_2]$ chelates with a tetrahedral MO_2S_2 core.

IR and NMR Spectroscopy

The IR spectrum of **1** in Nujol is similar to the spectrum of **2**. The absorption bands of the P=O group of the anionic forms **L** in complexes **1** and **2** are shifted by approximately 70 cm^{-1} to low frequencies relative to the band of the parent ligand **HL**. This confirms their participation in chelate formation. The signal for the NH proton is absent in the IR spectra of complexes **1** and **2**.

The main difference involves the absorption bands of the SCN group.[19,20] In the spectrum of a suspension of **1** in Nujol there is an intense absorption band at 1528 cm^{-1}, whereas in **2** the participation of sulfur atoms in dimer formation results in the occurrence of three intense absorption bands in the given area: 1536, 1576 and 1584 cm^{-1}. In a CCl_4 solution of complex **2** the bands merge into one with a maximum of 1536 cm^{-1}, which suggests the dissociation of the dimeric molecules.

The IR spectrum of **3** contains two bands for different phosphorus groups. Along with the above band corresponding to the **L** form, a strong P=O band is observed at 1240 cm^{-1} because of the bound neutral molecules of **HL**. Its frequency also decreases relative to that of the band of the free ligand; however, the shift is 12 cm^{-1}. The absorption band for the NH group at 3176 cm^{-1} also indicates the presence of **HL** molecules in complex **3**.

The $^{31}P\{^1H\}$ NMR signals of complexes **1** and **2** appear at δ = 5.7 and 3.0 ppm, respectively, and a down-field shift, relative to that of the free ligand **HL** (δ = –5.6 ppm), is observed. Full width at half peak maximum is in the range 1.0–5.0 Hz.

The ^1H NMR spectra contain a single set of signals for the $(i\text{PrO})_2P(O)$ and C_6H_5 protons. The *o*-phenyl proton signals in complexes **1** and **2** are shifted down-field. The signal for the NHP(O) group proton is absent in ^1H NMR spectra. This confirms the presence of the **HL** anionic form in the structures of complexes **1** and **2**.

The formation of dimeric structures in solution would lead to doubling or to exchange broadening of the signals in the NMR spectra. Distinction between the trailer and bridging ligand forms should be shown in the NMR spectra for ^{13}C and ^{31}P nuclei. Experimental evidence has shown that in both complexes **1** and **2** the ^{13}C and ^{31}P NMR spectra indicate that there is no doubling or exchange broadening of the signals for carbon and phosphorus atoms. Thus, the NMR spectroscopic data confirm that in $CDCl_3$ solution complexes **1** and **2** are exclusively in the monomeric form.

There are two singlet signals at δ = –6.0 and 3.7 ppm, which have identical integrated intensities, in the $^{31}P\{^1H\}$ NMR spectrum of complex **3**. The signal at δ = –6.0 ppm is in the region that is characteristic for neutral *N*-phosphorylated thioamides and thioureas, whereas the second signal corresponds to the amidophosphate environment in complexes of *N*-acylamidophosphate anions.

The ^1H NMR spectrum contains a double set of equal-intensity signals for the $(i\text{PrO})_2P(O)$ and C_6H_5 protons. The spectrum of complex **3** basically represents the sum of the spectra of ligand **HL** and complex **2** (Figure 1). The assignment of the ^1H NMR spectrum of compound **3** is executed by comparing the spectrum of **3** with those of **HL** and complex **2**. For a more exact reference of OCH proton signals of complex **3**, the spectrum of a mixture of **3** and **HL** was run at a molar ratio of 3:1. The increase in intensities of the low-field OCH group signal and the signal for the high-field *o*-C_6H_5 protons, concerning the neutral **HL** form, confirms the reference made by comparison of the spectra.

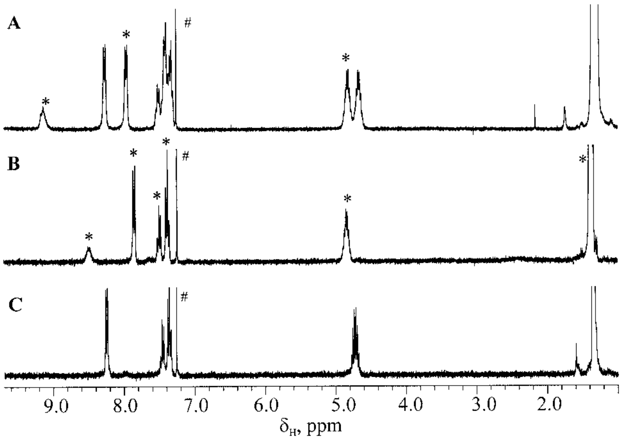


Figure 1. ^1H NMR spectra of complexes **3** (A), **2** (C) and **HL** (B). Signals of **HL** (free and in the structure of **3**) are marked * and a signal for the solvent #.

EI and ES Mass Spectrometry

The electron impact mass spectrum (EI-MS) of **1** contains the $[ZnL_2]^+$ structure molecular ion peak. The molecular ions of **2** $[Cd_2L_4]^+$ and **3** $[Cd(HL)_2L_2]^+$ are unstable under the measurement conditions, and the heaviest molecular ion observed in the spectra of **2** and **3** corresponds to the neutral $[CdL_2]^+$ complex core.

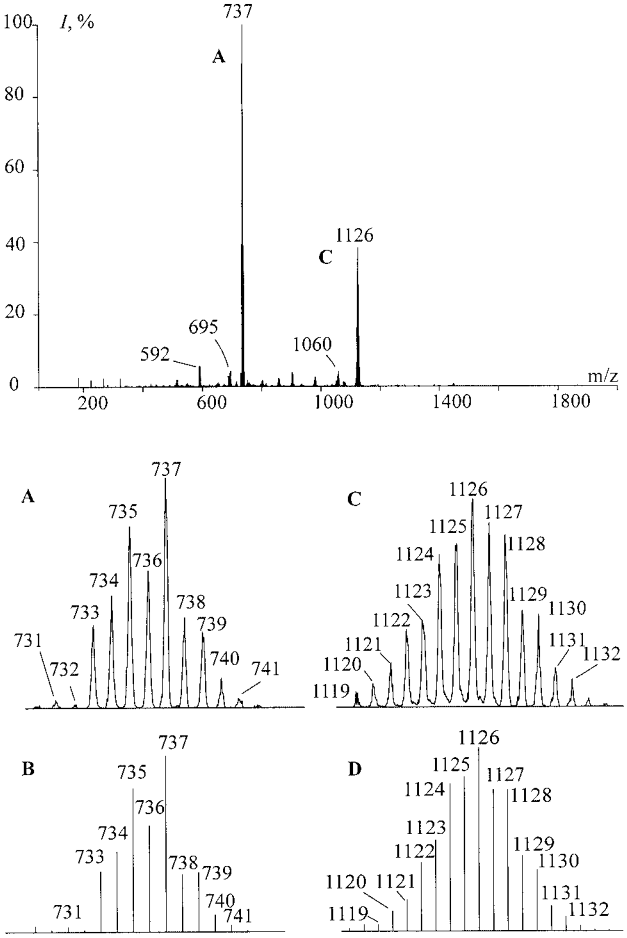


Figure 2. ES-MS spectra of complex **2**. Peak **A** is observed for the $[CdL_2 + Na]^+$ cation, pattern **B** is calculated for $C_{26}H_{38}CdN_2NaO_6P_2S_2$, peak **C** is observed for the $[Cd_2L_3]^+$ cation and pattern **D** is calculated for $C_{39}H_{57}Cd_2N_3O_9P_3S_3$.

ES-MS experiments (electrospray method) on complexes **1** and **2** show peaks for the molecular ions $[ML_2 + Na]^+$ and $[ML_2 + K]^+$. The cations $[ML_2 + H]^+$, on the contrary, are unstable. This is, apparently, connected to the separating of the **HL** molecule.

The ES-MS data of **2** (Figure 2) shows propensity to dimer formation. The intensity of the $[Cd_2L_3]^+$ peak in the electrospray spectrum of complex **2** is 38% and is maximal in a number of the investigated compounds. The $[Cd_2L_4 + Na]^+$ peak has an intensity of 0.8%.

The molecular ion peak of **3** is absent. Its electrospray spectrum contains all ions characteristic of the $[CdL_2]$ complex core: $[CdL_2 + H]^+$ (low intensity), $[CdL_2 + Na]^+$, $[CdL_2 + K]^+$, $[Cd_2L_3]^+$.

Crystal Structure of 1

According to the X-ray data, complex **1** is a spirocyclic chelate with a distorted tetrahedral ZnO_2S_2 core (Figure 3).

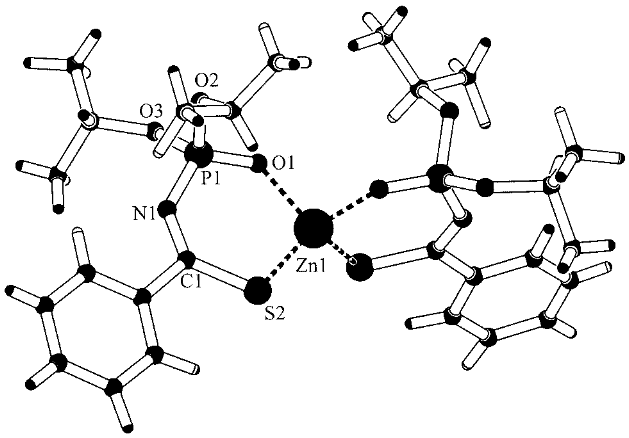


Figure 3. Molecular structure of complex **1**.

Table 1. Selected bond lengths [Å], and bond and torsion angles [°] for complex **1**.[a]

Bond lengths			
Zn1–S2	2.288(1)	P1–O1	1.492(2)
Zn1–O1	1.962(2)	P1–N1	1.614(2)
S2–C1	1.735(3)	N1–C1	1.285(3)
Bond angles			
S2–Zn1–O1	102.83(8)	O1–P1–N1	118.9(1)
S2–Zn1–S2_a	118.82(8)	Zn1–O1–P1	125.1(1)
S2–Zn1–O1_a	104.52(14)	P1–N1–C1	133.4(1)
O1–Zn1–O1_a	113.64(80)	S2–C1–N1	129.1(2)
Zn1–S2–C1	107.7(1)	S2–C1–C2	114.7(2)
Torsion angles			
O1–Zn1–S2–C1	1.4(1)	N1–P1–O1–Zn1	–21.2(2)
S2–Zn1–O1–P1	11.4(2)	O1–P1–N1–C1	–108.6(3)
Zn1–S2–C1–N1	–4.9(3)	P1–N1–C1–S2	–4.6(4)

[a] Symmetry transformations used to generate equivalent atoms: _a (–*x*, *y*, –*z* + 1/2).

Similarly to those of the [$Co^{II}L_2$] complex with the same ligand, investigated by us earlier,[21] the six-membered chelate rings are practically flat. The phosphorus atoms usually have a tetrahedral configuration in such compounds. Selected values of bond lengths, bond and torsion angles are given in Table 1.

Crystal Structure of 2

The X-ray data show that in a crystal form complex **2** is a centrosymmetric dimer. In contrast to the imidodiphosphinate complexes, the bond does not occur through the oxygen atoms of the P=O[12] groups, but through the sulfur atoms of the C=S groups of the deprotonated ligand **HL**. Complex **2** contains two types of ligand anions – tridentate bridging and didentate terminal (Figure 4).

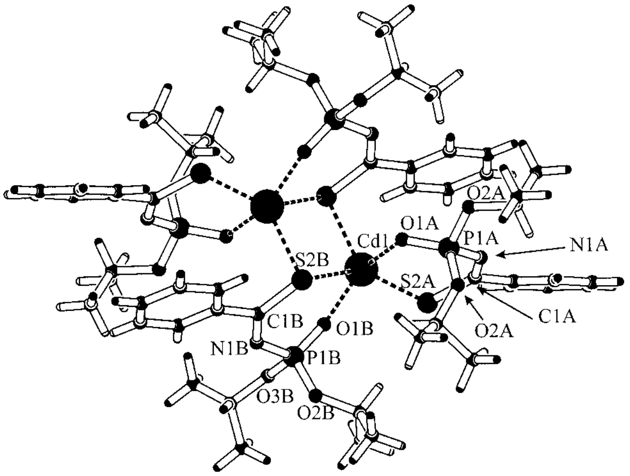


Figure 4. Molecular structure of complex **2**.

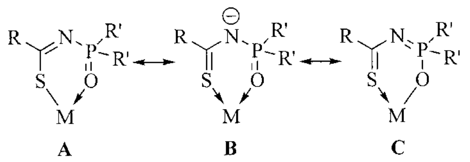
The Cd^{II} cations are in a distorted trigonal-bipyramidal environment (CdO_2S_3). The axial positions are occupied by the oxygen atoms of the P=O groups, and the sulfur atoms lie in its base. The Cd_2S_4 moiety is flat in the molecule of **2** (Table 2). Predictably, coordination bonds with the sulfur atoms of terminal ligands Cd01–S2A are, essentially, more than 0.16 Å shorter than with the bridging sulfur atoms Cd01–S2B. The lengths of the Cd–O bonds in the Cd^{II} cation's coordination sphere are practically equivalent, but the bond with the oxygen atom of the bridging ligand, Cd01–O1B, deviates from the normal to the Cd_2S_4 plane (O1A–Cd01–O1B 155°), while the Cd01–O1A bond is practically perpendicular to the Cd_2S_4 plane. The S2B–Cd01–S2B_a angle in the Cd_2S_4 plane is more than 50° sharper than S2A–Cd01–S2B.

The lengths of the bonds in the S–C–*N*–P–O backbone confirm the distinction in negative charge delocalisation mechanisms in bridging and terminal ligands. It is known that three tautomeric forms, A, B and C, contribute to the distribution of electronic density in six-membered chelates of (thioacylamido)phosphates (Scheme 2).

Table 2. Selected bond lengths [Å], and bond and torsion angles [°] for complex **2**.[a]

Bond lengths			
Cd01–S2A	2.5015(2)	P1A–O1A	1.444(2)
Cd01–S2B	2.6620(1)	P1A–N1A	1.616(5)
Cd01–O1A	2.313(3)	P1B–O1B	1.468(4)
Cd01–O1B	2.300(3)	P1B–N1B	1.625(5)
Cd01–S2B_a	2.5957(1)	N1A–C1A	1.283(7)
S2A–C1A	1.744(5)	N1B–C1B	1.278(7)
S2B–C1B	1.761(5)		
Bond angles			
S2A–Cd01–S2B	143.94(5)	Cd01–S2B–C1B	114.2(2)
S2A–Cd01–S2B_a	123.91(5)	Cd01–S2B–Cd01_a	87.86(4)
S2B–Cd01–S2B_a	92.14(4)	C1B–S2B–Cd01_a	96.4(2)
O1B–Cd01–S2B_a	105.9(1)	O1A–P1A–N1A	119.7(2)
S2A–Cd01–O1A	91.3(1)	O1B–P1B–N1B	120.6(2)
S2A–Cd01–O1B	85.0(1)	Cd01–O1A–P1A	125.2(2)
S2B–Cd01–O1A	83.46(9)	Cd01–O1B–P1B	128.8(2)
S2B–Cd01–O1B	85.33(9)	P1A–N1A–C1A	132.8(4)
O1A–Cd01–O1B	155.3(1)	P1B–N1B–C1B	130.4(4)
O1A–Cd01–S2B_a	96.4(1)	S2A–C1A–N1A	128.6(4)
Cd01–S2A–C1A	110.6(2)	S2B–C1B–N1B	127.6(4)
Torsion angles			
C1A–S2A–Cd01–O1A	–18.2(2)	C1B–S2B–Cd01–O1B	–167.73(19)
P1A–O1A–Cd01–S2A	–6.8(2)	P1B–O1B–Cd01–S2B	–19.3(3)
Cd01–O1A–P1A–N1A	–34.5(6)	Cd01–O1B–P1B–N1B	43.7(4)
C1A–N1A–P1A–O1A	–34.5(6)	C1B–N1B–P1B–O1B	–35.5(6)
N1A–C1A–S2A–Cd01	25.8(5)	N1B–C1B–S2B–Cd01	20.5(5)
S2A–C1A–N1A–P1A	–0.1(8)	S2B–C1B–N1B–P1B	–0.3(7)

[a] Symmetry transformations used to generate equivalent atoms: _a (1–*x*, 1 –*y*, 1 –*z*).



Scheme 2.

Displacement of electronic density on the sulfur atom in bridging ligands leads to the shortening of the C–N and P=O bonds and also to the lengthening of the P–N and C=S bonds because of the prevalence of the tautomeric form A. The P=O bond in these ligands is even shorter than in the free ligand molecule.[19] In the cases with terminal ligands, the contribution of forms B and C which leads to average bonds lengths in the cycle, is shown to a greater degree.

The dimer formation leads to a significant lengthening of the Cd–S bonds in six-membered chelate cycles of the bridging ligands. Therefore, these bonds are the longest in a number of compounds investigated by us, their lengths exceeding even those of the bridging Cd–S bonds connecting $[CdL_2]$ moieties in the structure of the dimer.

Crystal Structure of 3

According to the Cambridge Crystallographic Database, there are no structural analogues of complex **3** that involve *N*-acylamidophosphates or related chelators such as imidodiphosphinates and β-dicarbonyl compounds and Group IIB cations. The nearest analogue of complex **3** is described for $i\mathrm{Bu_2NC(S)NHC(O)C_6H_5}$ (**HQ**). The complex has the structure [Cd(HQ-*S*)(Q-*O*,*S*)$_2$] (**4**).[22] As in complex **2**, the Cd^{II} cation in complex **4** is in a distorted trigonal-bipyramidal $Cd(O^{ax})_2(S^{eq})_3$ environment.

The molecule of complex **3** in a crystal is located in a special position at the symmetry centre. The coordination geometry of the Cd^{II} atom is tetragonal bipyramidal (D_{2h}) (Figure 5). Isostructural complexes of Co^{II} and Ni^{II} with **HL** exist and have been synthesised by us previously.[21]

The equatorial positions of the bipyramid are occupied by two *N*-phosphorylthiobenzamide anions, bonded through sulfur atoms and oxygen atoms of the phosphoryl groups. The six-membered Cd–O–P–*N*–C–S cycle has a half-chair conformation; the O–P–*N*–C–S backbone is flat (Table 3). The ligands are in a *trans* configuration. A negative charge delocalisation in the S–C–*N*–P–O moiety also takes place in this case. This leads to the contraction of the C–N and P–N bonds and also to the lengthening of the C=S bonds, but the P=O bond lengths decrease by 0.013 Å relative to that of the free ligand **HL**. As in complex **2**, this observation results from a significant preference of the form A (Scheme 2).

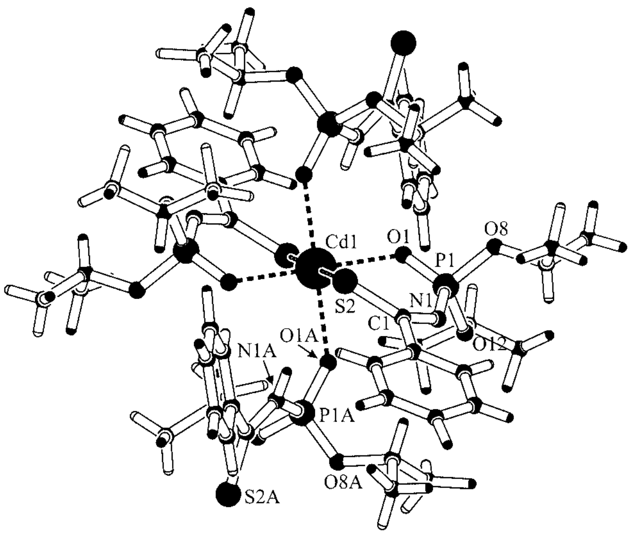


Figure 5. Molecular structure of complex **3**.

Table 3. Selected bond lengths [Å], and bond and torsion angles [°] for complex **3**.[a]

Bond lengths			
Cd1–S2	2.546(2)	P1–N1	1.611(3)
Cd1–O1	2.273(2)	P1A–O1A	1.467(2)
Cd1–O1A	2.372(2)	P1A–N1A	1.677(3)
S2–C1	1.687(3)	N1–C1	1.289(3)
S2A–C1A	1.637(3)	N1A–C1A	1.363(4)
P1–O1	1.444(2)	N1A–H1A	0.81(3)
Bond angles			
S2–Cd1–O1	89.74(8)	O1A–P1A–N1A	106.4(1)
S2–Cd1–O1A	88.76(7)	Cd1–O1–P1	120.6(1)
S2–Cd1–S2_a	180.00	Cd1–O1A–P1A	137.0(1)
O1–Cd1–O1A	89.25(8)	P1–N1–C1	134.6(2)
O1–Cd1–O1_a	180.00	P1A–N1A–C1A	131.1(2)
O1A–Cd1–O1A_a	180.00	N1–C1–C2	116.7(2)
Cd1–S2–C1	105.1(1)	S2–C1–N1	128.6(2)
O1–P1–N1	122.3(1)	S2–C1–C2	114.6(2)
N1A–C1A–C2A	114.9(2)	S2A–C1A–N1A	123.4(2)
S2A–C1A–C2A	121.8(2)		
Torsion angles			
O1–Cd1–S2–C1	–39.8(1)	O1–P1–N1–C1	–15.6(3)
O1A–Cd1–S2–C1	49.5(1)	O1A–P1A–N1A–C1A	177.2(2)
S2–Cd1–O1–P1	39.2(1)	N1A–P1A–O1A–Cd1	–30.1(2)
O1A–Cd1–O1–P1	–49.5(1)	P1–N1–C1–C2	–174.5(2)
S2–Cd1–O1A–P1A	68.8(2)	P1–N1–C1–S2	5.9(4)
Cd1–S2–C1–N1	27.8(3)	P1A–N1A–C1A–S2A	0.1(4)
N1–P1–O1–Cd1	–18.9(2)	P1A–N1A–C1A–C2A	179.1(2)

[a] Symmetry transformations used to generate equivalent atoms: _a $(2 - x, -y, 2 - z)$.

Neutral ligand molecules are coordinated in the axial positions through the oxygen atoms of the phosphoryl groups. The conformation of the neutral molecules and the lengths of C–N and P–N bonds in a crystal are practically identical to those of free *N*-phosphorylthiobenzamide **HL**. Some lengthening of the P=O and C=S bonds is observed, which results from the displacement of electronic density in the S–C–*N*–P–O moiety on the oxygen atom of the phosphoryl group.

There are two intramolecular NH···S bonds between the neutral and anionic ligands in the crystal of complex **3**. The hydrogen bond parameters are as follows: N(1A)–H(1A)···S(2) (–*x*, –*y*, –*z*), *d*(N–H) 0.81(3) Å, *d*(H···S) 2.72(3) Å, *d*(N···S) 3.499(3) Å, ∠(N–H···S) 164(2)°.

Conclusion

Comparison of the data of complex compounds of cadmium(II), known from the literature, with acylureas and imidodiphosphinates shows that the cadmium(II) cation in the structure of the complex CdO_2S_2 core exhibits properties of a "universal" Lewis acid. Its coordination environment can be expanded because of interaction with both "soft" and "hard" bases. Differences in modes of interaction are apparently related to the distribution of electronic density in the ligand molecules.

These features of complexes with a CdO_2S_2 core can be used in the future for the creation of new types of building blocks for polynuclear metal-containing macrocyclic compounds. We have recently reported the synthesis of close structural analogues of the ligand **HL** that contain crown ether moieties and their complexes with Ni^{II} and Cu^{I}.[11,23–25] The cavities of the macrocycles in the given structures remain free and are capable of participating in secondary coordination. We suppose that the combination of the CdO_2S_2 core and crown ether in the molecule will allow one to synthesise compounds that are able to bind cations, by the crown ether moiety, and anions and neutral molecules, by the electrophilic CdO_2S_2 core. Such kinds of compounds are of interest as agents for molecular recognition and membrane transport.

Experimental Section

Physical Measurements: Infrared spectra (Nujol) were recorded with a Specord M-80 spectrometer in the range 400–3600 cm^{-1}. NMR spectra were obtained on a Varian Unity-300 NMR spectrometer at 25 °C. ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded at 299.948, 121.420 and 75.429 MHz, respectively. Chemical shifts are reported with reference to $SiMe_4$ (^1H and $^{13}C\{^1H\}$) and H_3PO_4 ($^{31}P\{^1H\}$). Electron ionisation mass spectra were measured on a TRACE MS Finnigan MAT instrument. The ionisation energy was 70 eV. The substance was injected directly into the ion source at 150 °C. Heating was carried out in a programmed mode from 35–200 °C at a rate of 35 °C/min. Electrospray ionisation mass spectra were measured with a Thermo Finnigan LCQ mass spectrometer on a 10^{-6} M solution in a $CHCl_3/CH_3OH$ mixture (1:1 v/v). The speed of a sample submission was 3 µL/min. The ionisation energy was 4.1 kV. The capillary temperature was 210 °C. Elemental analyses were performed on a Perkin–Elmer 2400 CHN microanalyser.

Synthesis of $(\textit{i}PrO)_2P(O)NHC(S)C_6H_5$ (HL): *N*-Diisopropoxyphosphorylthiobenzamide was prepared according to previously described methods.[26] M.p. 134 °C. ^1H NMR ($CDCl_3$): $\delta = 1.34$ (d, $^3J_{H,H} = 5.9$ Hz, 6 H, CH_3), 1.38 (d, $^3J_{H,H} = 6.2$ Hz, 6 H, CH_3), 4.83 (d. sept, $^3J_{POCH} = {}^3J_{H,H} = 6.1$ Hz, 2 H, OCH), 8.49 [s, 1 H, NHP(O)], 7.37–7.42 (m, 2 H, *m*-H, C_6H_5), 7.49–7.54 (m, 1 H, *p*-H, C_6H_5), 7.85–7.88 (m, 2 H, *o*-H, C_6H_5), 8.49 (s, 1 H, NH) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -5.6$ ppm. IR: $\tilde{\nu} = 3104$ (NH), 1500 (S=C–N), 1012 (POC), 1252 (P=O) cm^{-1}.

Synthesis of $[ZnL_2]$ (1): A suspension of **HL** (1.505 g, 5 mmol) in aqueous ethanol (20 mL) was mixed with an ethanol solution of potassium hydroxide (0.28 g, 5 mmol). An aqueous (20 mL) solution of $ZnCl_2$ (0.381 g, 2.8 mmol) was added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred at room temperature for a further 3 h and left overnight. The resulting complex was extracted with dichloromethane, washed with water and dried with anhydrous $MgSO_4$. The solvent was then removed in vacuo. A colourless precipitate was isolated from dichloromethane by *n*-hexane. Yield (based on the metal salt): 0.865 g (52%). M.p. 92 °C. ^1H NMR ($CDCl_3$): $\delta = 1.34$ (d, $^3J_{H,H} = 5.9$ Hz, 12 H, CH_3), 1.35 (d, $^3J_{H,H} = 5.8$ Hz, 12 H, CH_3), 4.72 (d. sept, $^3J_{POCH} = 7.6$ Hz, $^3J_{H,H} = 6.2$ Hz, 4 H, OCH), 7.35–7.40 (m, 4 H, *m*-H, C_6H_5), 7.45–7.50 (m, 2 H, *p*-H, C_6H_5), 8.26–8.29 (m, 4 H, *o*-H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 24.5 (CH_3), 73.5 (OCH), 128.4 (*o*-C, C_6H_5), 129.3 (*m*-C, C_6H_5), 132.6 (*p*-C, C_6H_5), 143.8 (*ipso*-C, C_6H_5), 195.2 (C=S) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 5.7 ppm. IR: $\tilde{\nu} = 1528$ (SCN), 996 (POC), 1152 (P=O) cm^{-1}. EI-MS: *m/z* (%) = 664 (8) $[M]^+$, 301 (8) $[HL]^+$. ES-MS (positive ion): *m/z* (%) = 687 (100) $[M + Na]^+$, 703 (10) $[M + K]^+$, 1032 (1) $[M_2L_3]^+$, 1353 $[M_2L_4 + Na]^+$. $C_{26}H_{38}N_2O_6P_2S_2Zn$ (666.05): calcd. C 46.87, H 5.77, N 4.18; found C 46.88, H 5.75, N 4.19.

Synthesis of $[Cd_2L_4]$ (2) and $[Cd(HL)_2L_2]$ (3): A suspension of **HL** (1.806 g, 6 mmol) in aqueous ethanol (20 mL) was mixed with an ethanol solution of potassium hydroxide (0.336 g, 6 mmol). An aqueous (20 mL) solution of $Cd(CH_3COO)_2\cdot 2H_2O$ (0.798 g, 3 mmol) was added dropwise to the resulting potassium salt under vigorous stirring. The mixture was stirred at room temperature for a further 3 h and left overnight. The resulting complex was extracted with dichloromethane, washed with water and dried with anhydrous $MgSO_4$. The solvent was then removed in vacuo. The residue was extracted by *n*-hexane. A hexane insoluble deposit was recrystallised from a dichloromethane/*n*-hexane mixture, and complex **2** was isolated. Complex **2** was obtained as colourless crystals. Yield (based on the metal salt): 0.918 g (43%). M.p. 102 °C. ^1H NMR ($CDCl_3$): 1.40 (d, $^3J_{H,H} = 6.4$ Hz, 24 H, CH_3), 4.82 (d. sept, $^3J_{POCH} = 7.5$ Hz, $^3J_{H,H} = 6.4$ Hz, 4 H, OCH), 7.34–7.39 (m, 4 H, *m*-H, C_6H_5), 7.44–7.49 (m, 2 H, *p*-H, C_6H_5), 8.23–8.26 (m, 4 H, *o*-H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 24.5 (CH_3), 73.2 (OCH), 128.4 (*o*-C, C_6H_5), 129.5 (*m*-C, C_6H_5), 132.4 (*p*-C, C_6H_5), 144.3 (*ipso*-C, C_6H_5), 193.9 (C=S) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 3.0 ppm. IR: $\tilde{\nu} = 1536$, 1576, 1584 (SCN), 1015 (POC), 1184 (P=O) cm^{-1}. EI-MS: *m/z* (%) = 714 (34) $[ML_2]^+$, 301 (15) $[HL]^+$. ES-MS (positive ion): *m/z* (%) = 715 (2) $[ML_2 + H]^+$, 737 (100) $[ML_2 + Na]^+$, 753 (2) $[ML_2 + K]^+$, 1126 (38) $[M_2L_3]^+$, 1449 (0.8) $[M_2L_4 + Na]^+$. $C_{52}H_{76}Cd_2N_4O_{12}P_4S_4$ (1424.12): calcd. C 43.80, H 5.34, N 3.97; found C 43.81, H 5.33, N 3.98.

At the solvent-removal stage (hexane soluble), product **3** was isolated. Complex **3** was obtained as yellow crystals. Yield (based on the metal salt): 0.355 g (18%). M.p. 94 °C. ^1H NMR ($CDCl_3$): 1.29 (d, $^3J_{H,H} = 6.1$ Hz, 36 H, CH_3, L + HL), 1.35 (d, $^3J_{H,H} = 6.1$ Hz, 12 H, CH_3, L), 4.67 (d. sept, $^3J_{POCH} = {}^3J_{H,H} = 6.2$ Hz, 4 H, OCH, L), 4.82 (d. sept, $^3J_{POCH} = {}^3J_{H,H} = 6.4$ Hz, 4 H, OCH, HL), 7.47–7.74 (m, 12 H, *m*-H + *p*-H, C_6H_5, L + HL), 7.95–7.98 (m, 4 H, *o*-H, C_6H_5, HL), 8.26–8.28 (m, 4 H, *o*-H, C_6H_5, L), 9.15 [s, 2 H, NHP(O)] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): –6.0 (HL), 3.7 (L) ppm. IR: $\tilde{\nu} = 1536$ (SCN), 1013 (POC), 1168 (L, P=O), 1240 (HL, P=O) cm^{-1}. EI-MS: *m/z* (%) = 714 (29) $[M - 2HL]^+$, 301 (73) $[HL]^+$. ES-MS (positive ion): *m/z* (%) = 715 (2) $[ML_2 + H]^+$, 737 (100) $[ML_2 +$

Table 4. Crystal data, data collection and refinement details for complexes **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_{26}H_{38}N_2O_6P_2S_2Zn$	$C_{52}H_{78}Cd_2N_6O_{10}P_4S_4$	$C_{52}H_{78}CdN_4O_{12}P_4S_4$
Formula mass	666.05	1424.12	1315.70
Space group	*C*2/*c* (molecule in special position on the axis 2)	$P\bar{1}$ (molecule in special position)	$P2_1/n$ (molecule in special position)
a [Å]	18.324(9)	10.569(3)	13.375(9)
b [Å]	9.730(9)	10.941(2)	12.858(7)
c [Å]	18.24(2)	15.560(4)	18.594(7)
α [°]	90	74.11(2)	90
β [°]	93.35(7)	72.92(3)	90.71(6)
γ [°]	90	79.93(3)	90
V [Å^3]	3247(5)	1645.5(8)	3197(3)
Z	4	1	2
$D_{calcd.}$ (mg/m^3)	1.36	1.44	1.37
F(000)	1392	732	1372
Crystal colour	colourless	colourless	colourless
Crystal form	prismatic	prismatic	prismatic
Crystal size [mm]	0.3 × 0.3 × 0.3	0.4 × 0.3 × 0.2	0.2 × 0.3 × 0.2
Radiation [Å]		1.54184	0.71073
Temperature [K]	293	293	293
Scan mode	*ω*	*ω*	*ω*
Recording range θ_{max} [°]	70.07	57.19	6.29
Absorption correction	*ψ*-scan	*ψ*-scan	*ψ*-scan
μ [cm^{-1}]	35.14	77.46	28.11
Scan speed (°/min)	variable, 1–16.4	variable, 1–16.4	variable, 1–16.4
No. of recorded reflections	3373	3726	7205
No. of independent reflections with $I \geq 3\sigma(I)$	3016	3695	5022
No. of independent reflections with $F^2 \geq 2\sigma(F^2)$	2999	3239	6606
R (%)	0.0449	0.0557	0.033
R_w (%)	0.1236	0.1362	0.083
S	1.061	1.047	1.011

Na]$^+$, 753 (2) [ML$_2$ + K]$^+$, 1126 (7) [M$_2$L$_3$]$^+$. $C_{52}H_{78}CdN_4O_{12}P_4S_4$ (1315.70): calcd. C 47.44, H 6.01, N 4.29; found C 47.42, H 6.03, N 4.28.

Crystal Structure Determination and Refinement: The X-ray diffraction data for the crystals of **1**–**3** were collected on a CAD4 Enraf–Nonius automatic diffractometer using graphite-monochromated Mo-K_α (0.71073 Å) and Cu-K_α (1.54184 Å) radiation. The crystal data, data collection and the refinement are given in Table 4. The stability of the crystals and the experimental conditions were checked every 2 h using three control reflections, while the orientation was monitored every 200 reflections by centring two standards. No significant decay was observed. An empirical absorption correction based on *ψ*-scans was applied. The structure was solved by direct methods using the SIR[27] program and refined by the full-matrix least-squares using the SHELXS-97[28] program. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms for compounds **1** and **3** were located from a subsequent difference map and refined isotropically in the final cycles. The hydrogen atoms for compound **2** were included in calculated positions with thermal parameters 30% larger than the atom to which they were attached. All calculations were performed on a PC using the WinGX[29] program. Cell parameters, data collection and data reduction were performed on an Alpha Station 200 computer using the MolEN[30] program. All figures were made using the program PLATON.[31]

CCDC-286427, CCDC-286426 and CCDC-286425 contain the supplementary crystallographic data for this paper. 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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