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Cd^{2+} Complexation with $P(CH_2OH)_3$, $OP(CH_2OH)_3$, and $(HOCH_2)_2PO_2^-$: Coordination in Solution and Coordination Polymers

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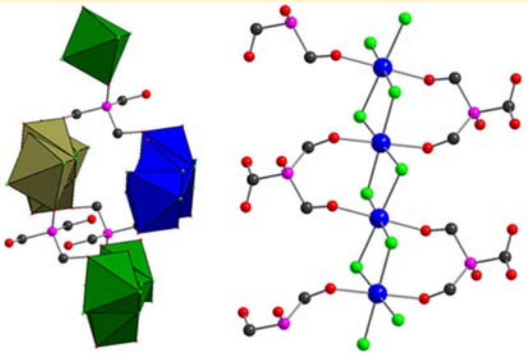
Supporting Information

ABSTRACT: The coordination of Cd^{2+} with $P(CH_2OH)_3$ (THP) in methanol was followed by ^{31}P and ^{111}Cd NMR techniques. A cadmium-to-phosphine coordination ratio of 1:3 has been established, and effective kinetic parameters have been calculated. Air oxidation of THP in the presence of $CdCl_2$ at room temperature produces coordination polymer $^{3}_{\infty}[Cd_3Cl_6(OP(CH_2OH)_3)_2]$ (**1**). The same oxidation reaction at 70 °C gives another coordination polymer, $_{\infty}[CdCl_2(OP(CH_2OH)_3)]$ (**2**). Complexes **1** and **2** are the first structurally characterized complexes featuring $OP(CH_2OH)_3$ as a ligand that acts as a linker between Cd atoms. The addition of $NaBPh_4$ to the reaction mixture gives coordination polymer $_{\infty}[Na_2CdCl_2(O_2P(CH_2OH)_2)_2(H_2O)_3]$ (**3**) with $(HOCH_2)_2PO_2^-$ as the ligand. Coordination polymers **1**−**3** have been characterized by X-ray analysis, elemental analysis, and IR spectroscopy.



INTRODUCTION

Cadmium (as Cd^{2+}) displays rich coordination chemistry and readily forms complexes with various N-, O-, and S-donor ligands.[1−13] This versatility is due to adaptable coordination geometry around Cd^{2+} and to the borderline position of Cd^{2+} in terms of hard−soft acid−base (HSAB) dualism. Recent developments in the field of cadmium coordination chemistry include the creation of Cd^{2+}-based coordination networks featuring noncentrosymmetric metal−organic frameworks (MOF) with nonlinear-optical (NLO) properties, MOFs with photochemical building units, luminescent complexes, selective gas-sorption behavior, etc. Organic ligands with N- and O-donor centers are typically used in these preparations.[1−13] The S-donor (as well as Se- and Te-donor) ligands are excellent auxiliary groups for stabilizing Cd_xQ_y "nanoclusters" (Q = S, Se, Te) with 10−32 Cd atoms, which show interesting photophysical properties.[14−19] Cadmium complexes with phosphines have received less attention, even though large clusters such as $[Cd_{32}Se_{14}(SePh)_{36}(PPh_3)_4]$ are stabilized by phosphine coordination. Extensive studies on the coordination of CdX_2 (X = Cl, Br, I, NCS, OR, SR, NO_3, RCOO, RCS_2) with PR_3 (R = Ph, tolyl, Cy, Et, Bu, $SiMe_3$) and phospholes were carried out. The 1:1 and 1:2 complexes are typical products of such complexation.[20−32] Few studies of the coordination of Cd^{2+} to functionalized phosphines have been reported. Complexes with $Ph_2PC(S)NHPh$ and diphenylphosphinebenzenethiolate have been prepared.[33,34] The coordination of $P(CH_2COO)_3^{3-}$ and $(OOCH_2)_2PCH_2CH_2P(CH_2COO)_2^{4-}$ with Cd^{2+} leads to the formation of unique coordination polymers assembled through both Cd−P and Cd−O coordination.[35,36] In this paper, we report our study on the coordination of Cd^{2+} with tris(hydroxymethyl)phosphine [$P(CH_2OH)_3$, THP] in methanol by ^{31}P and ^{111}Cd NMR at various temperatures. In this study, we also have found that THP is easily oxidized in the presence of Cd^{2+} with formation of the oxide $(HOCH_2)_3P{=}O$ and the phosphinate $(HOCH_2)_2PO_2^-$ (HMP), which proved to be efficient ligands for the formation of coordination polymers of variable dimensionality.

EXPERIMENTAL SECTION

Materials and Methods. All manipulations with air-sensitive free $P(CH_2OH)_3$ (THP) were performed under argon. Complexes with coordinated THP and its oxide are air-stable and can be handled in air. Methanol was purified by distillation over magnesium turnings prior to use. THP, $NaBPh_4$, $CdCl_2{\cdot}2.5H_2O$, and $[Cd(H_2O)_6](ClO_4)_2$ (Sigma-Aldrich) were used as supplied. ^{31}P (202 MHz), ^{111}Cd (106 MHz), and ^{113}Cd (111 MHz) NMR spectra were recorded on a Bruker Avance 500 spectrometer in D_2O over a temperature range of 173−300 K. ^{31}P NMR chemical shifts were referenced to an 85% solution of H_3PO_4 in D_2O as the external standard. ^{113}Cd NMR shifts were referenced to a 1 M solution of $Cd(ClO_4)_2$ in D_2O as the external standard.

*$^{3}_{\infty}[Cd_3Cl_6(OP(CH_2OH)_3)_2]$ (**1**).* $CdCl_2{\cdot}2.5H_2O$ (0.228 g, 1.00 mmol) was dissolved in 10 mL of methanol, then THP (0.248 g, 2.00 mmol) was added, and the resulting colorless solution was stirred for 3 days under argon. Then the solution was transferred into an open vial and left for crystallization. After 2 weeks, light-yellow crystals of **1** were collected and washed with cold Et_2O. Yield: 0.07 g (26%). Anal. Calcd

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Table 1. X-ray Experimental Details[a]

	1	2	3
Crystal Data			
chemical formula	$C_3H_9Cd_{1.50}Cl_3O_4P$	$C_3H_9CdCl_2O_4P$	$C_4H_{18}CdCl_2Na_2O_{11}P_2$
M_r	415.02	323.37	533.40
cryst syst, space group	triclinic, $P\bar{1}$	monoclinic, $P2_1/m$	orthorhombic, *Pbcn*
temperature (K)	150(2)	150(2)	150(2)
a, *b*, *c* (Å)	6.9101(3), 8.7737(3), 9.5432(4)	6.9570(2), 7.3639(2), 8.8093(3)	18.5304(5), 8.8733(3), 10.0502(3)
α, β, γ (deg)	72.226(1), 87.036(1), 67.136(1)	90, 105.518(1), 90	90, 90, 90
V (Å^3)	506.19(4)	434.85(2)	1652.51(9)
Z	2	2	4
F(000)	394	312	1056
radiation type	Mo Kα	Mo Kα	Mo Kα
μ (mm^{-1})	4.10	3.27	1.94
cryst size (mm^3)	0.16 × 0.16 × 0.10	0.32 × 0.25 × 0.20	0.28 × 0.05 × 0.04
Data Collection			
diffractometer	Bruker Nonius X8 Apex CCD diffractometer		
abs corrn	multiscan *SADABS* (Bruker-AXS, 2004)		
T_{min}, T_{max}	0.560, 0.684	0.421, 0.561	0.613, 0.927
no. of measd, indep, and obsd [$I > 2\sigma(I)$] reflns	7088, 3647, 3336	3179, 955, 881	9452, 1692, 1548
R_{int}	0.014	0.016	0.022
θ values (deg)	$\theta_{max} = 32.6$, $\theta_{min} = 2.3$	$\theta_{max} = 26.4$, $\theta_{min} = 2.4$	$\theta_{max} = 26.4$, $\theta_{min} = 2.5$
ranges of *h*, *k*, and *l*	$-10 \leq h \leq 10$, $-13 \leq k \leq 12$, $-13 \leq l \leq 14$	$-8 \leq h \leq 8$, $-5 \leq k \leq 9$, $-11 \leq l \leq 11$	$-14 \leq h \leq 23$, $-11 \leq k \leq 11$, $-12 \leq l \leq 11$
Refinement			
R1 [$F^2 > 2\sigma(F^2)$], wR2 (F^2), S	0.016, 0.041, 1.04	0.024, 0.059, 1.10	0.019, 0.052, 1.04
no. of reflns	3647	955	1692
no. of param	115	65	109
no. of restraints	0	6	2
H-atom treatment	H-atom parameters constrained		
weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0174P)^2 + 0.4512P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.016P)^2 + 2.3519P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0265P)^2 + 2.3495P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.93, −0.48	1.26, −0.84	0.99, −0.50

[a] Computer programs: *APEX2* (Bruker-AXS, 2004), *SAINT* (Bruker-AXS, 2004), *SHELXS97* (Sheldrick, 1998), *SHELXL97* (Sheldrick, 1998), *SHELXTL* (Bruker-AXS, 2004), and *CIFTAB-97* (Sheldrick, 1998).

for $C_6H_{18}O_8Cd_3P_2Cl_6$: C, 8.68; H, 2.36; Cl, 27.69. Found: C, 8.55; H, 2.14; Cl, 27.58. IR (ν, cm^{-1}): 399 m, 498 m, 574 w, 667 w, 726 m, 813 m, 860 m, 905 s, 1025 s (P═O, C−OH), 1121 s (P═O, C−OH), 1184 m (P═O, C−OH), 1238 w, 1304 w, 1368 s, 1419 s, 1575 w, 2040 w, 2635 m, 2791 m, 2906 m, 2969 m, 3024 m, 3295 m (OH), 3502 s (OH).

$_\infty$[CdCl$_2$OP(CH$_2$OH)$_3$] **(2)**. $CdCl_2 \cdot 2.5H_2O$ (0.228 g, 1.00 mmol) was dissolved in 10 mL of a methanol/water solution (1:1, v/v), then THP (0.248 g, 2.00 mmol) was added, and the resulting colorless solution was stirred for 3 days under argon at room temperature. Then the solution was heated in air for 4 h at 70 °C and left for crystallization in an open vial. After 3 weeks, colorless crystals of **2** were collected and washed with cold Et_2O. Yield: 0.09 g (29%). Anal. Calcd for $C_3H_9O_4Cl_2PCd$: C, 11.14; H, 2.81; Cl, 24.25. Found: C, 11.19; H, 2.88; Cl, 24.33. IR (ν, cm^{-1}): 490 w, 525 w, 695 w, 742 m, 879 m, 1046 m (P═O, C−OH), 1131 m (P═O, C−OH), 1386 w, 1434 m, 1628 m, 1729 w, 2025 s, 2920 s, 3059 s, 3433 (OH) br.

$_\infty$[Na$_2$CdCl$_2$(O$_2$P(CH$_2$OH)$_2$)$_2$(H$_2$O)$_3$] **(3)**. $CdCl_2 \cdot 2.5H_2O$ (0.228 g, 1.00 mmol) was dissolved in 10 mL of a methanol/water mixture (1:1, v/v), then THP (0.248 g, 2.00 mmol) was added, and the resulting colorless solution was stirred for 3 days under argon at room temperature. Then a solution of $NaBPh_4$ (0.684 g, 2.00 mmol) in 5 mL of a methanol/water mixture (1:1, v/v) was added, and the solution was boiled 6 h in an air atmosphere and left in an open vial. After 5 weeks, colorless crystals of **2** were collected and washed with cold Et_2O. Yield: 0.11 g (21%). Anal. Calcd for $C_4H_{18}O_4Cl_2P_2CdNa_2$: C, 9.01; H, 3.40; Cl, 13.29. Found: C, 8.93; H, 3.34; Cl, 13.17. IR (ν, cm^{-1}): 468 m, 668 w, 850 m, 894 m, 1046 s (PO_2, C−OH), 1073 s (PO_2, C−OH), 1132 s (═O), 1206 m, 1326 w, 1423 av, 1587 m, 2059 w, 2645 w, 2830 m, 2902 m, 3358 br (OH).

X-ray Crystallography. Crystallographic data and refinement details are given in Table 1. The data sets for **1**−**3** were collected on a Bruker X8 Apex CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) by doing φ and ω scans of narrow (0.5°) frames at 150(2) K. The structures were solved by direct methods and refined by a full-matrix least-squares treatment against $|F|^2$ in an anisotropic approximation with the *SHELXTL* program set.[37] Absorption corrections were applied empirically with the *SADABS* program.[38] All non-H atoms of the main structural units were refined anisotropically. The H atoms were refined in their geometrically calculated positions; a riding model was used for this purpose. Further details may be obtained from the Cambridge Crystallographic Data Center upon quoting depository numbers CCDC 882964−882966. Copies of this information may be obtained free of charge from http://www.ccdc.cam.ac.uk.

■ RESULTS AND DISCUSSION

NMR Study of Complexation between Cd^{2+} and THP.

The addition of THP to a solution of $CdCl_2$ in 4:1 and 16:1 molar ratios at room temperature leads to the appearance of a new sharp signal in the ^{31}P NMR spectrum at −14 ppm, which is downshifted from the signal of the free THP at −26 ppm (Figures 1 and 2). The absence of Cd−P splitting satellites indicates a rapid exchange process at room temperature between free and coordinated THP. Lowering the temperature

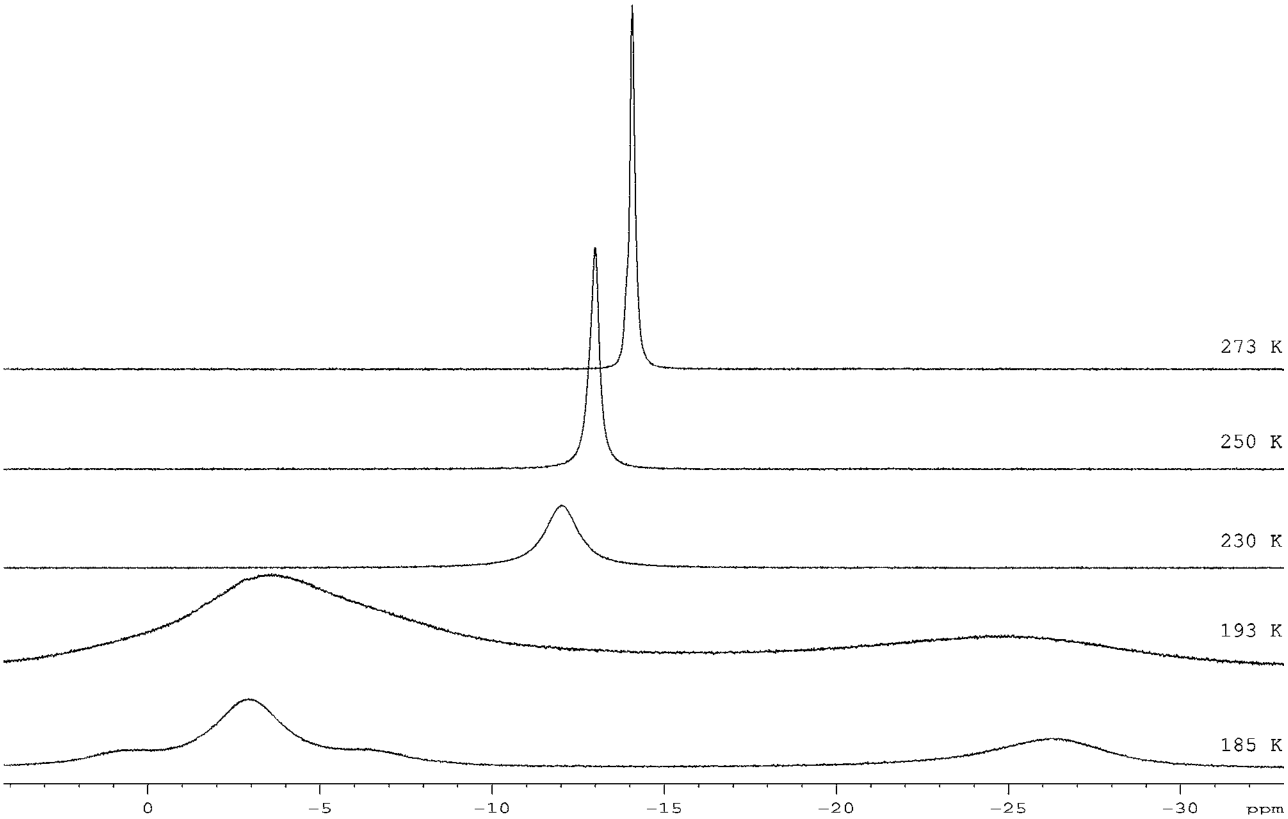

Figure 1. ^{31}P NMR spectra of a methanol-d_4 solution of $CdCl_2$ and THP with concentration ratio Cd:P = 0.1:0.4 M at various temperatures.

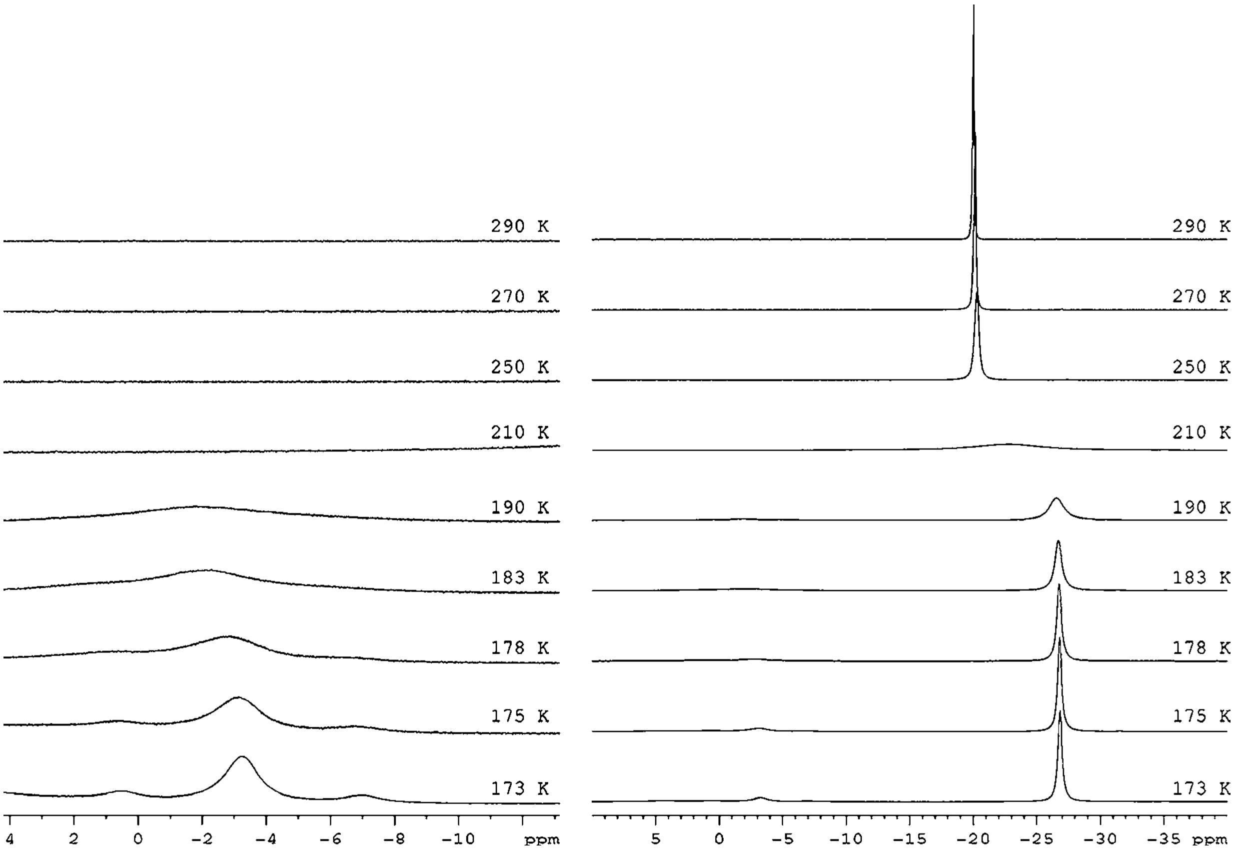

Figure 2. ^{31}P NMR spectra of a methanol-d_4 solution of $CdCl_2$ and THP with concentration ratio Cd:P = 0.1:1.6 M.

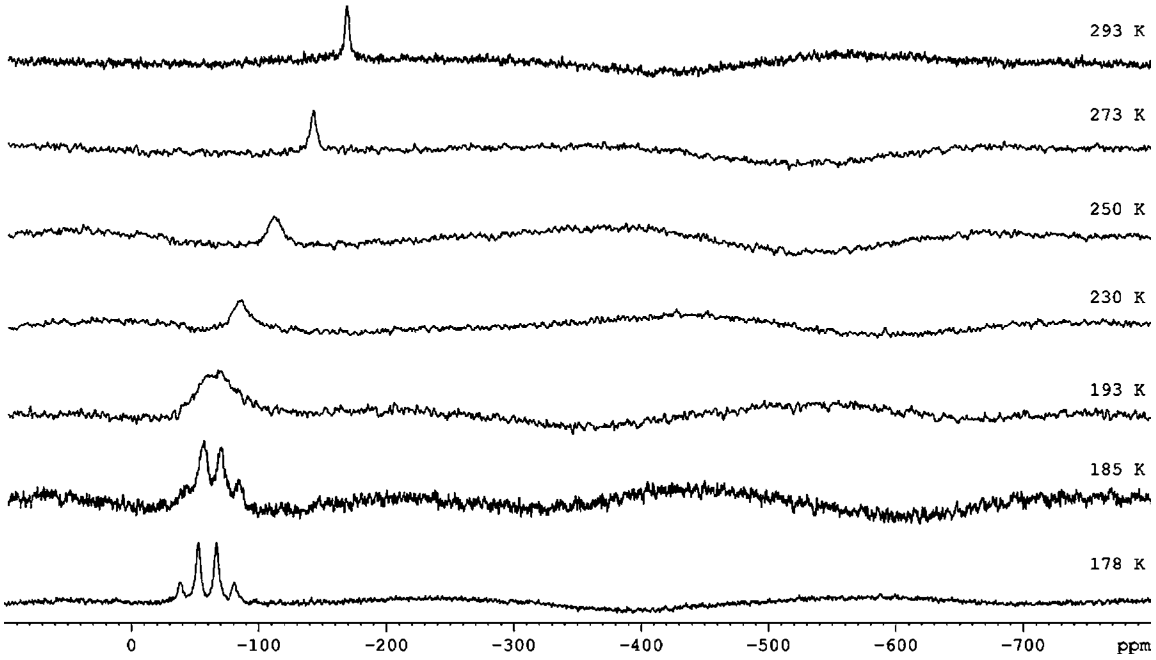

Figure 3. ^{113}Cd NMR spectra of a methanol-d_4 solution of $CdCl_2$ and THP with concentration ratio Cd:P = 0.1:0.4 M.

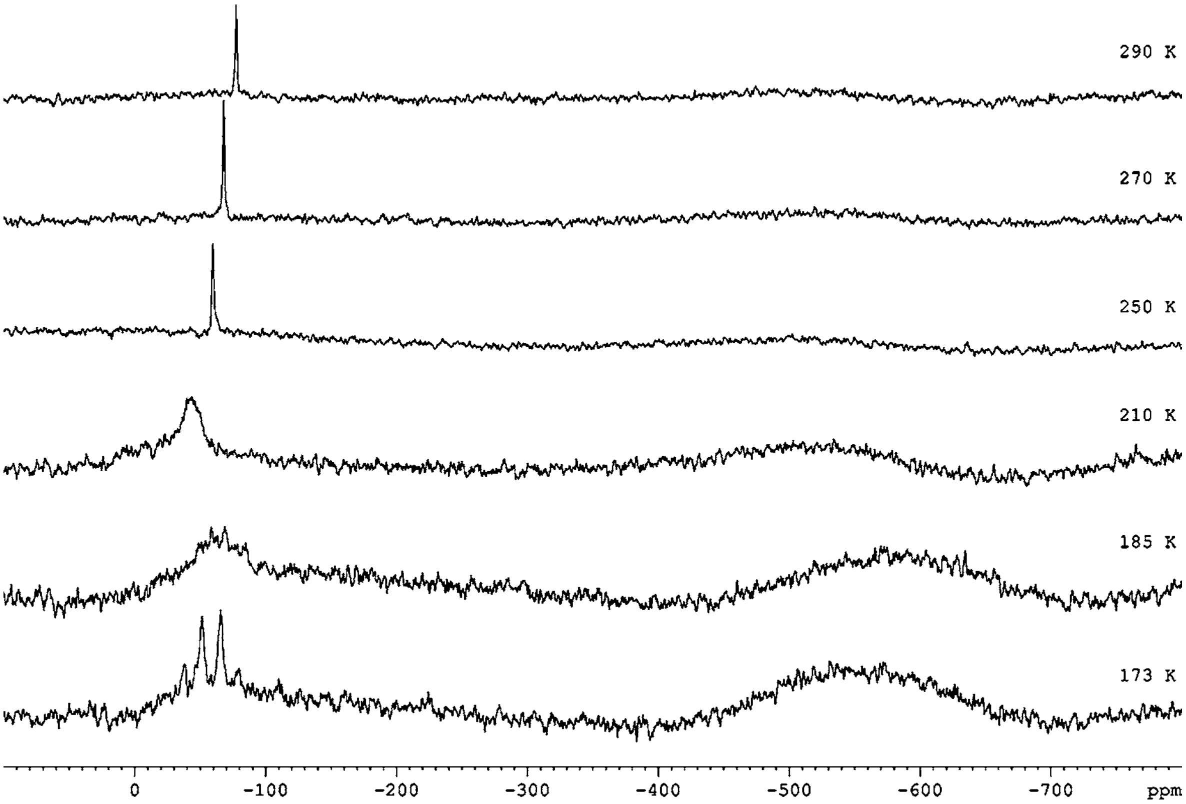

Figure 4. ^{113}Cd NMR spectra of a methanol-d_4 solution of $CdCl_2$ and THP with concentration ratio Cd:P = 0.1:1.6 M.

causes signal broadening followed by the reappearance of the sharp line from free THP (below 183 K) and the appearance of a broad triplet indicating Cd−P bonding. Similar behavior is observed in ^{113}Cd NMR (Figure 3, 4). Only significant lowering of the temperature down to 173 K leads to the appearance of a well-resolved quartet in the ^{113}Cd NMR spectrum, centered at −59 ppm, which corresponds to a 1:3 Cd^{2+}/THP complexation product, formulated as $Cd(P(CH_2OH)_3)_{3(solv.)}{}^{2+}$. In accordance with preferable coordination number 4 for Cd^{2+} in the phosphine environment, it possibly contains coordinated Cl^- or CH_3OH molecules to occupy the fourth coordination position. As can be seen from the NMR data, $Cd(P(CH_2OH)_3)_{3(solv.)}{}^{2+}$ is the only detectable product (Table 2). As expected, chemical shifts in ^{111}Cd and ^{113}Cd NMR spectra coincide, but because ^{113}Cd is 10% more sensitive, only ^{113}Cd NMR spectra will be used in the

Table 2. ^{31}P and ^{113}Cd NMR Chemical Shifts and $^{1}J_{\text{Cd-P}}$ Coupling Constant Data at Concentration Ratio Cd:P = 0.1:0.4 M at Various Temperatures

T, K	$J_{^{113}\text{Cd}-^{31}\text{P}}$, Hz	$\delta(^{113}\text{Cd})$, ppm	$\delta(^{31}\text{P})$, ppm
178	1527	−59.3	
185	1371	−60.4	−2.7, −26.3
193	979	−63.2	−3.6, −24.8
230		−80.7	−12.0
250		−109.1	−13.0
273		−140.4	−14.0
293		−166.2	−14.0

discussion here. Figures 3 and 4 show the temperature dependence of the ^{113}Cd signals in the methanol-d_4 solution of $CdCl_2$ and THP with concentration ratio $[Cd^{2+}]$:[THP] = 0.1:0.4 M (1:4 Cd/P molar ratio). In an earlier study on the complexation of CdX_2 with PBu_3, only the formation of 1:2 complexes $[CdX_2(PBu_3)_2]$ was observed by ^{113}C and ^{31}P NMR. Similar to our study, it was found that well-resolved signals of the complexes appeared only at 178 K.[42] The ^{113}Cd−^{31}P values are in good agreement with those reported for $[CdX_2(PBu_3)_2]$ (X = Cl, Br, I) (1300−1600 Hz).[39] The signal shape broadening with a temperature increase is due to a rapid chemical exchange between uncomplexed and complexed species and has been reported for the CdX_2/PBu_3 system. The signal shift is due to a chemical equilibrium at a given concentration ratio of the system components. The temperature dependence of the $^{1}J_{\text{Cd-P}}$ coupling constant can be due to changes in the solvent exchange rate and has been reported for Cd−P and Hg−P coordination.[40] Only a large excess of THP (16-fold relative to cadmium) is able to completely shift the chemical equilibrium toward the formation of $Cd(P(CH_2OH)_3)_{3(\text{solv.})}{}^{2+}$. This has been proven by the temperature dependence of the signals corresponding to ^{113}Cd and ^{31}P NMR signals of $Cd(P(CH_2OH)_3)_{3(\text{solv.})}{}^{2+}$ in the methanol-d_4 solution of $CdCl_2$ and THP at concentration ratio $[Cd^{2+}]$:[THP] = 0.1:1.6 M (1:16 Cd/P molar ratio; Figure 4 and Table 3). As can be seen from Figure 4, even under a large excess of THP, the complexation is limited by the formation of a 1:3 complex. The absence of doublet, triplet, or quintet signals at different concentration ratios shows that $Cd(P(CH_2OH)_3)_{3(\text{solv.})}{}^{2+}$ is the only thermodynamically stable species in this system. It is worth mentioning that all previously reported complexes of cadmium with phosphines contained only one or two coordinated phosphine ligands per Cd atom.[20−32] Unfortunately, our attempts to isolate a solid product from this reaction failed. As a result of the quantitative examination of the ^{31}P and ^{113}Cd NMR signal line shapes in the frame of dynamic NMR techniques applied to chemical exchange,[41] the chemical exchange rate constants (k) were estimated at various temperatures. By linear regression analysis of the dependence of $\ln(k/T)$ on $1/T$ using the Eyring equation, the effective activation enthalpy and activation entropy values for eq 1 were obtained as $\Delta H^{\ddagger} = 59.3 \pm 9.2$ kJ mol^{-1} and $\Delta S^{\ddagger} = 113.1 \pm 31.5$ J mol^{-1} K^{-1}, respectively.

$$\ln\left[\frac{k(T)}{T}\right] = -\frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R} + \ln\left(\frac{k_B}{h}\right) \quad (1)$$

Table 3. ^{31}P and ^{113}Cd NMR Chemical Shifts and $^{1}J_{\text{Cd-P}}$ Coupling Constant Data at Concentration Ratio Cd:P = 0.1:1.6 M at Various Temperatures

T, K	$J_{^{113}\text{Cd}-^{31}\text{P}}$, Hz	$\delta(^{113}\text{Cd})$, ppm	$\delta(^{31}\text{P})$, ppm
173	1570	−58.0	−3.25, −26.8
185	1150	−64.5	−2.2, −26.7
190			−2.1, −26.6
210		−42.8	−22.8
250		−59.3	−20.3
270		−68.0	−20.1
290		−77.4	−20.0

Relatively big errors in the calculated activation parameters are accounted for by simplification of the stepwise equilibration process, which is seen by NMR as a single one-stage process. Large positive values of the activation parameters are in agreement with the decrease in the coordination number of Cd^{2+} on going from $Cd_{(\text{solv.})}{}^{2+}$ to $Cd(P(CH_2OH)_3)_{3(\text{solv.})}{}^{2+}$. It has been mentioned that alcohols (such as EtOH)[42] can successfully compete with phosphines for coordination placed at Cd^{2+}. This can explain the absence of the $[Cd(THP)_4]^{2+}$ signal at Cd/P ratios higher than 1:3. These findings indicate that the preference for a hard or soft ligand (in our case, for CH_3OH or THP, respectively) not only is a function of the nature of the metal ion (in terms of HSAB) or solvent but also may be temperature-dependent, even though the interpretation of such a behavior might not be straightforward.

Preparation and Crystal Structures of 1−3. The crystal structure of **1** contains infinite chains formed by Cd atoms and bridging chlorine ligands (Figure 5) that account for the $CdCl_2$ stoichiometry. The chains are connected into a 3D structure by $OP(CH_2OH)_3$ (THPO) ligands acting as tritopic ligands. There are two sorts of Cd atoms: atoms of one sort (Cd1) have two trans-coordinated THPO ligands (both in P=O coordination mode), and atoms of the other sort (Cd2) coordinate two hydroxo groups of two different THPO ligands in the cis position. In this way, each THPO molecule coordinates with its two OH groups to Cd2 and with the P=O group to Cd1; hence, each ligand connects three $CdCl_2$ chains. The structure may be interpreted as chains of "$CdCl_2$" with alternating square-planar and nonplanar (derived from an octahedron by the removal of two cis vertices) $CdCl_4$ units interconnected by tritopic THP linkers into a 3D framework (Figure 5) so that each THP ligand connects three different chains using one P=O and two CH_2OH groups. The Cd−Cl bond length (2.58−2.61 Å; Table 4) is typical for such kinds of coordination polymers (e.g., 2.62 Å for $\{[Cd(\text{D,L-alanine})Cl_2]\cdot H_2O\}$,[42] 2.63 Å for $_{\infty}[Cd(\text{4-aminobutanoic acid})Cl_2]$,[43] and 2.61 Å $[Cd(\text{L-alanine})Cl_2]$[44]). The Cd−O distances (2.34−2.38 Å) can, in turn, be compared to the Cd−O distances found in $_{\infty}\{[Cd(HOC_2H_4OH)Cl_2]_3\cdot HOC_2H_4OH\}$[45] (2.40 Å), $^{2}_{\infty}[Cd\{(CH_3OC_2H_4O)_2C_2H_4\}Cl_2]$[46] (2.41 Å), $_{\infty}[Cd_3Cl_6(C_{15}H_{15}NO_2)_2(CH_3OH)_2]$[47] ($C_{15}H_{15}NO_2$ = 2-methoxy-6-[(4-methylphenyl)iminomethyl]phenol; 2.40 Å), and $^{3}_{\infty}[Cd(O(C_2H_4)_2O)Cl_2]$[48] (2.40 Å).

In the crystal structure of $_{\infty}[CdCl_2OP(CH_2OH)_3]$ (**2**), infinite chains of Cd atoms bridged by chloride ligands run along b axis (Figure 6). In contrast to the structure of **1**, in **2** all Cd atoms are identical and each THPO ligand coordinates two adjacent Cd atoms from the same chain with two CH_2OH groups in a bridging manner, while other potential coordination sites (P=O and CH_2OH) participate only in hydrogen bonding with other chains. One OH group that is not coordinated to a Cd atom is disordered over two positions to

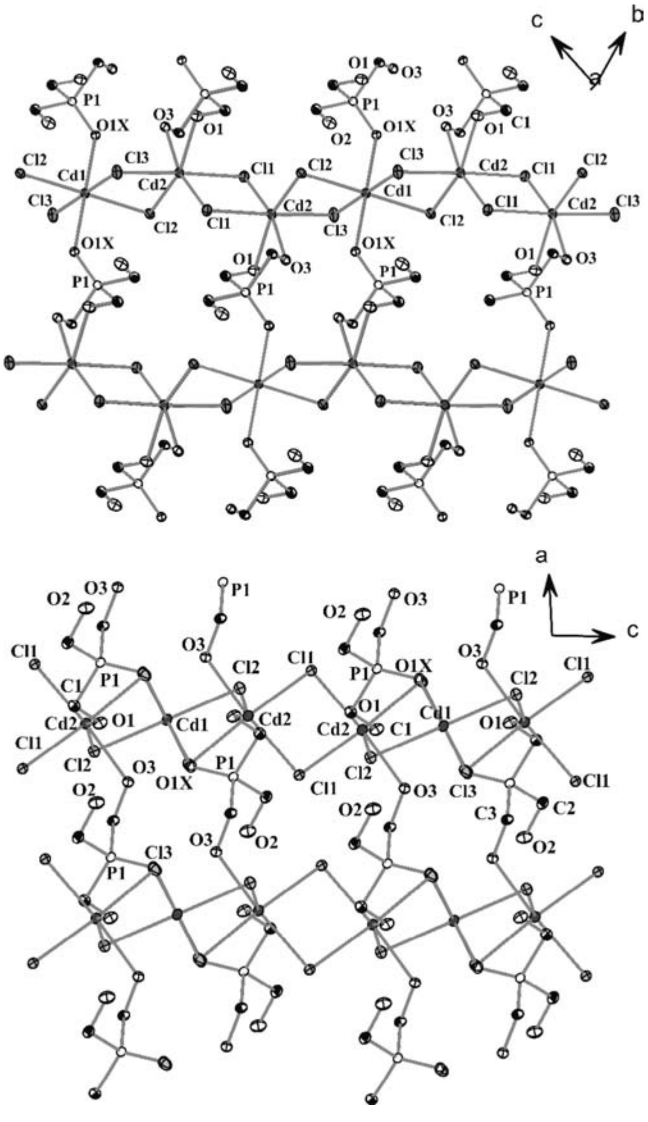

Figure 5. Structures of **1** along the axes *a* (top) and *b* (bottom). Ellipsoids are shown with 50% probability.

avoid unnaturally short contacts between neighboring chains. The average Cd−Cl bond length is 2.58 Å, and the average value of the Cd−O bond length is 2.37 Å (Table 5), expectedly close to the values observed in **1**. To the best of our knowledge, no crystal structures of a THPO complex hitherto have been reported.

Table 4. Selected Geometric Parameters for 1 (Å and deg)[a]

Cl1−Cd2$^{\mathrm{i}}$	2.6074(4)	O1X−Cd1$^{\mathrm{iii}}$	2.3378(11)
Cl3−Cd2$^{\mathrm{ii}}$	2.5781(4)	O1−Cd2$^{\mathrm{iv}}$	2.3548(13)
Cd1−Cl2	2.6154(4)	Cd1−O1X$^{\mathrm{v}}$	2.3379(11)
Cd1−Cl2$^{\mathrm{ii}}$	2.6154(4)	Cd1−O1X$^{\mathrm{vi}}$	2.3379(11)
Cd1−Cl3$^{\mathrm{ii}}$	2.6005(4)	Cd2−O1$^{\mathrm{vii}}$	2.3549(13)
Cd1−Cl3	2.6005(4)	Cd2−O3	2.4087(12)
Cd2−Cl1	2.5584(4)	P1−O1X	1.5161(12)
Cd2−Cl1$^{\mathrm{i}}$	2.6074(4)	P1−C1	1.8216(17)
Cd2−Cl2	2.5806(4)	P1−C2	1.8193(17)
Cd2−Cl3$^{\mathrm{ii}}$	2.5781(4)	P1−C3	1.8164(16)
Cl2−Cd1−Cl2$^{\mathrm{ii}}$	179.999(1)	Cl1−Cd2−Cl2	111.541(14)
Cl3$^{\mathrm{ii}}$−Cd1−Cl2	84.639(13)	Cl1−Cd2−Cl3$^{\mathrm{ii}}$	91.858(14)
Cl3−Cd1−Cl2	95.361(13)	Cl2−Cd2−Cl1$^{\mathrm{i}}$	95.064(13)
Cl3$^{\mathrm{ii}}$−Cd1−Cl2$^{\mathrm{ii}}$	95.361(13)	Cl3$^{\mathrm{ii}}$−Cd2−Cl1$^{\mathrm{i}}$	175.967(14)
Cl3−Cd1−Cl2$^{\mathrm{ii}}$	84.638(13)	Cl3$^{\mathrm{ii}}$−Cd2−Cl2	85.801(13)
Cl3$^{\mathrm{ii}}$−Cd1−Cl3	180.0	O1X$^{\mathrm{v}}$−Cd1−O1X$^{\mathrm{vi}}$	179.998(1)
Cl1−Cd2−Cl1$^{\mathrm{i}}$	84.158(13)	O1$^{\mathrm{vii}}$−Cd2−O3	72.25(4)

[a] Symmetry code(s): (i) $-x+2, -y, -z+1$; (ii) $-x+2, -y+1, -z$; (iii) $x+1, y-1, z$; (iv) $x+1, y, z$; (v) $x-1, y+1, z$; (vi) $-x+3, -y, -z$; (vii) $x-1, y, z$.

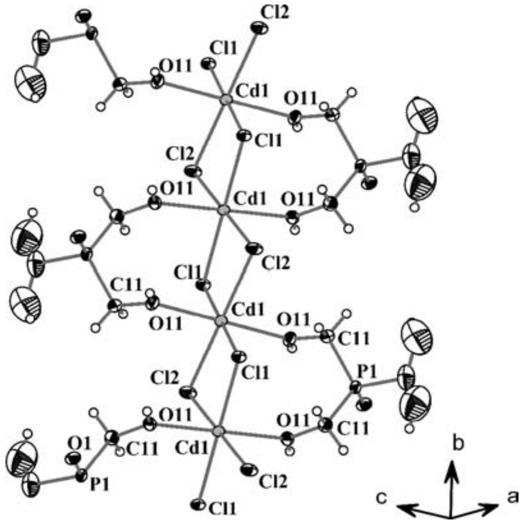

Figure 6. Structure of **2**. Ellipsoids are shown with 50% probability. Terminal OH groups of THPO have disordering in two positions.

Table 5. Selected Geometric Parameters for 2 (Å and deg)[a]

Cl1−Cd1$^{\mathrm{i}}$	2.5819(9)	Cd1−O11$^{\mathrm{ii}}$	2.365(2)
Cl2−Cd1$^{\mathrm{i}}$	2.5729(9)	Cd1−O11	2.365(2)
Cd1−Cl1	2.5819(9)	P1−O1	1.508(4)
Cd1−Cl1$^{\mathrm{ii}}$	2.5819(9)	P1−C11$^{\mathrm{iii}}$	1.815(4)
Cd1−Cl2$^{\mathrm{ii}}$	2.5729(9)	P1−C11	1.815(4)
Cd1−Cl2	2.5729(9)	P1−C13	1.830(8)
Cl1−Cd1−Cl1$^{\mathrm{ii}}$	180.0	Cl2−Cd1−Cl1$^{\mathrm{ii}}$	92.04(3)
Cl2$^{\mathrm{ii}}$−Cd1−Cl1	92.04(3)	Cl2$^{\mathrm{ii}}$−Cd1−Cl2	180.00(7)
Cl2−Cd1−Cl1	87.96(3)	O11$^{\mathrm{ii}}$−Cd1−O11	180.0
Cl2$^{\mathrm{ii}}$−Cd1−Cl1$^{\mathrm{ii}}$	87.96(3)		

[a] Symmetry code(s): (i) $-x, y+{}^{1}/_{2}, -z+2$; (ii) $-x, -y, -z+2$; (iii) $x, -y+{}^{1}/_{2}, z$.

Another coordination polymer, **3**, has a complicated crystal structure. It is based upon chains that are formed by bridging the $CdCl_2$ units by the anionic bis(hydroxymethyl)phosphinate $(HOCH_2)_2PO_2^-$ (HMP) ligands. Only phosphoryl groups participate in coordination, leaving the $-CH_2OH$ arms free. This arrangement is further strengthened by the incorporation of Na^+ cations. In the resulting arrangement, four HMP ligands connect two Na^+ and one Cd^{2+} into triangular "building blocks" (Figure 7) of composition $\{(H_2O)_2Na_2Cd(\mu_2\text{-}H_2O)(\mu_3\text{-}O_2P(CH_2OH)_2)_2(\mu_2\text{-}O_2P(CH_2OH)_2)_2\}$ curiously resembling transition-metal clusters of the type $[M_3(\mu_3\text{-}X)_2(\mu_2\text{-}Y)_3L_6]$ but, obviously, without M···M bonding.[49] Similar architectures are also found in the $\{Zr_2Cd(\mu_3\text{-}OPr^i)_2(\mu_2\text{-}OPr^i)_3\}$ units found in this work.[50] The $-CH_2OH$ arms remain free from coordination to Na^+. The Cd−O and Cd−Cl bond lengths are unexceptional and are listed in Table 6. Each HMP anion plays the double role of a μ_3-bridged ligand in one triangle unit and a μ_2-bridged ligand in another, forming polymeric chains along the

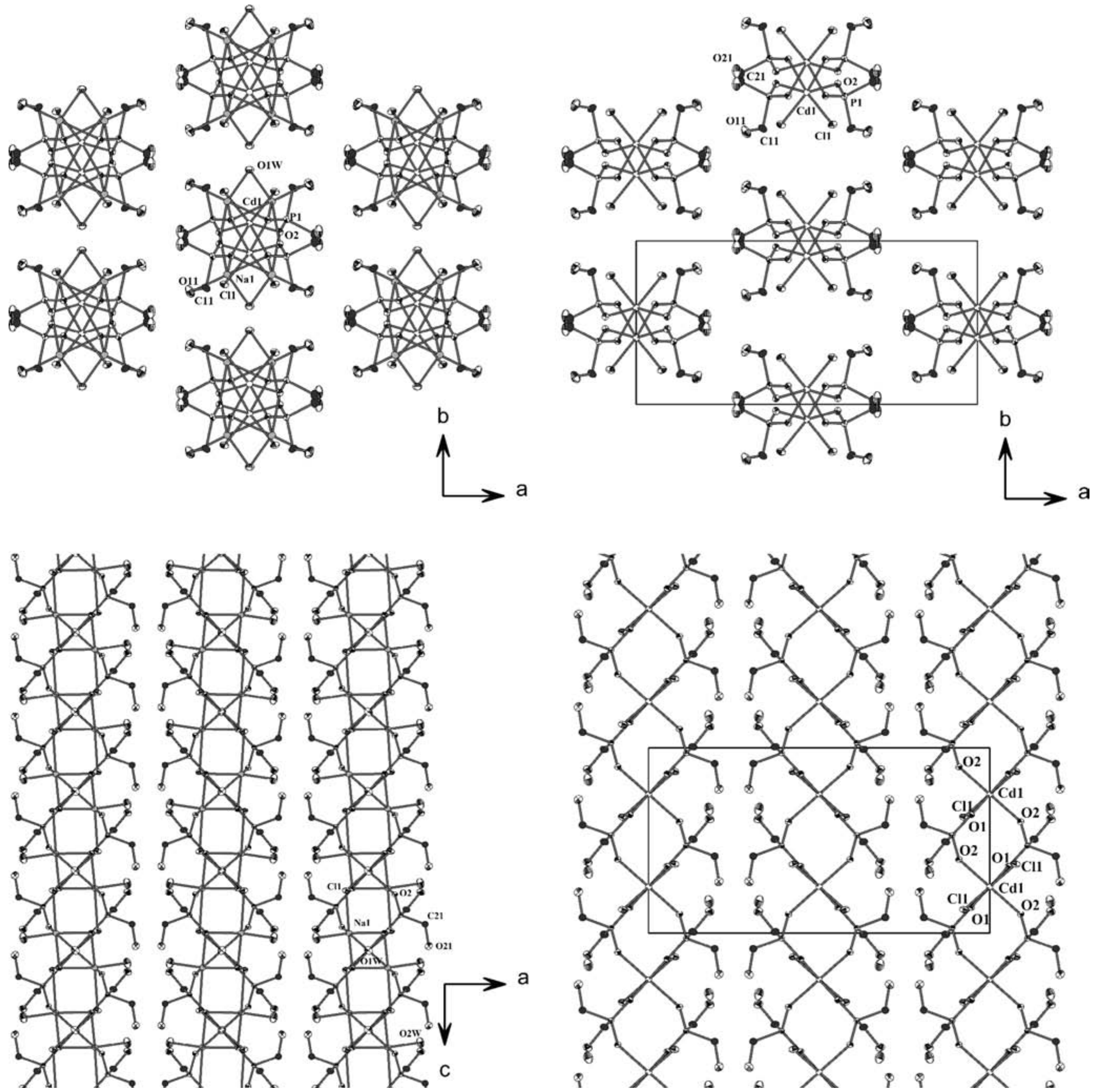

Figure 7. Structure of **3** viewed along the *c* axis with Na (top left), along the *c* axis without Na (top right), along the *b* axis with Na (bottom left), and along the *b* axis without Na (bottom right). Ellipsoids are shown with 50% probability.

crystallographic *c* axis (Figure 8). These chains are connected by hydrogen bonds from the CH_2OH groups and by terminal water molecules coordinated to the Na^+ cations. Ligand HMP seems to be very versatile and can play very different structural roles. In a copper(II) complex, $[Cu(HMP)_2(H_2O)_2]$,[51] it acts as a bidentate chelating ligand and forms five-membered chelate rings, which become involved in the coordination of an O atom from the PO_2 group and the O atom of one of the CH_2OH arms. In the structure of $[Sr(HMP)_2]$, the ligands are tetratopic, so that all four O atoms participate in the formation of a 3D network.[52] Both P═O and CH_2OH groups are involved in coordination in $Ln((O_2P(CH_2OH)_2)_3$ (Ln = La, Pr, Nd, Er, Lu), which are also coordination polymers.[52,53] The only complex of cadmium(II) with a diorganylphosphinate ligand, $[Cd((NH_3CH_2)_2PO_2)(H_2O)_2Cl_2]Cl_2$, features monodentate coordination of positively charged zwitterionic $(^+NH_3CH_2)_2PO_2^-$ ligands.[54]

The THPO and HMP ligands found in the structures of **1**−**3** were formed by the in situ oxidation of air-sensitive THP. The formation of THP is straightforward, and the formation of HMP is accounted for by the equilibrium

$$P(CH_2OH)_3 = HP(CH_2OH)_2 + CH_2O$$

followed by the in situ oxidation of $HP(CH_2OH)_2$ by O_2 into $^-O_2P(CH_2OH)_2$. Alternatively, HMP and its acid can be obtained by reacting hypophosphite $H_2PO_2^-$ with formaldehyde, CH_2O.[55]

Table 6. Selected Geometric Parameters for 3 (Å and deg)[a]

Cd1−Cl1	2.5586(6)	P1−C21	1.823(2)
Cd1−Cl1^{i}	2.5586(6)	O1W−Na1^{i}	2.3953(19)
O2−Cd1^{ii}	2.2893(15)	O1−Na1^{i}	2.4751(17)
Cd1−O1^{i}	2.3513(15)	O2−Na1^{iv}	2.4404(18)
Cd1−O1	2.3513(15)	Na1−O1W	2.3953(19)
Cd1−O2^{ii}	2.2893(15)	Na1−O1	2.4452(17)
Cd1−O2^{iii}	2.2893(15)	Na1−O1^{i}	2.4751(17)
P1−O1	1.5192(15)	Na1−O2W	2.294(2)
P1−O2	1.5214(16)	Na1−O2^{iii}	2.4404(18)
P1−C11	1.815(2)		
Cl1−Cd1−Cl1^{i}	94.08(3)	O2^{ii}−Cd1−O1	81.33(5)
O1^{i}−Cd1−O1	79.55(7)	O2^{iii}−Cd1−O1	80.33(5)
O2^{ii}−Cd1−O1^{i}	80.33(5)	O2^{ii}−Cd1−O2^{iii}	156.06(8)
O2^{iii}−Cd1−O1^{i}	81.33(5)		

[a] Symmetry code(s): (i) $-x + 1, y, -z + {}^{3}/_{2}$; (ii) $-x + 1, -y, -z + 2$; (iii) $x, -y, z - {}^{1}/_{2}$; (iv) $x, -y, z + {}^{1}/_{2}$.

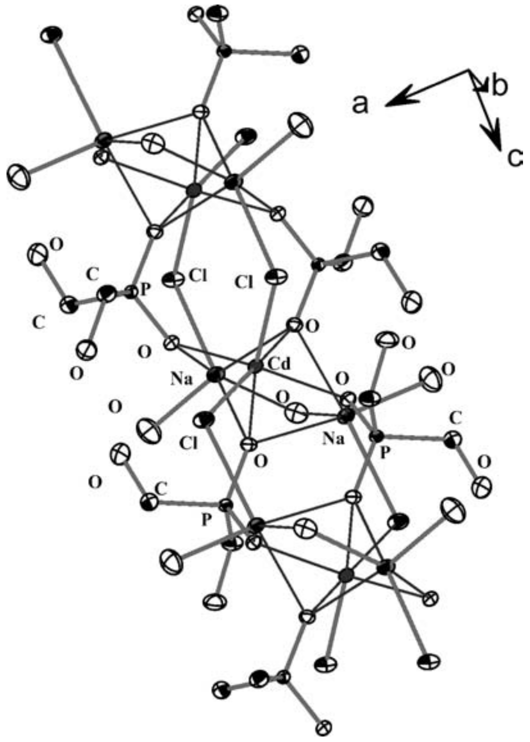

Figure 8. Triangular {Na_2Cd} "building blocks" in the crystal structure of 3. Ellipsoids are shown with 50% probability.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data for compounds **1**−**3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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