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Syntheses, Solid-State Structures, and Solution Studies by VT ^{31}P NMR of $[Zn\{Se_2P(OEt)_2\}_2]_\infty$ and $[Zn_2\{Se_2P(O^iPr)_2\}_4]$[†]

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Complexes $[Zn\{Se_2P(OEt)_2\}_2]_\infty$ (**1**) and $[Zn_2\{Se_2P(O^iPr)_2\}_4]$ (**2**) are prepared from the reaction of $Zn(ClO_4)_2{\cdot}6H_2O$ and $(NH_4)[Se_2P(OR)_2]$ (R = Et and ^{i}Pr) in a molar ratio of 1:2 in deoxygenated water at room temperature. Positive FAB mass spectra show *m*/*z* peaks at 968.8 ($Zn_2L_3^+$) and 344.8 (ZnL^+) for **1** and *m*/*z* at 1052.8 ($Zn_2L_3^+$) for **2**. ^{1}H NMR spectra exhibit chemical shifts at δ 1.43 and 4.23 ppm for **1** and 1.41 and 4.87 ppm for **2** due to Et and ^{i}Pr group of dsep ligands. While the solid-state structure of compound **1** is a one-dimensional polymer via symmetrically bridging dsep ligands, complex **2** in the crystalline state exists as a dimer. In both **1** and **2**, zinc atoms are connected by two bridging dsep ligands with an additional chelating ligand at each zinc atom. The dsep ligands exhibit bimetallic biconnective (μ_2, η^2) and monometallic biconnective (η^2) coordination patterns. Thus, each zinc atom is coordinated by four selenium atoms from two bridging and one chelating dsep ligands and the geometry around zinc is distorted tetrahedral. The Zn–Se distances range between 2.422 and 2.524 Å. From variable-temperature ^{31}P NMR studies it has been found that monomer and dimer of the complex are in equilibrium in solution via exchange of bridging and chelating ligands. However, at temperature above 40 °C the complex exists as a monomer and shows a very sharp peak while with lowering of the temperature the percentage of dimer increases gradually at the expense of monomer. Below –90 °C the complex exists as a dimer and two peaks are observed with equal intensities which are due to bridging and chelating ligands. ^{77}Se NMR spectra of both complexes at –30 °C exhibit three doublets due to the presence of monomer and dimer in solution.

Introduction

In general, bridging chalcogenolato ligands complexes of group 12 metals consist of polymeric structures and metal ions are tetrahedrally coordinated.[1] However, the degree of association in these compounds is sensitive to the steric requirements of the chalcogenolato ligands.[2] For example, the solid-state structure for zinc compound containing O,O′-dialkyl dithiphosphate ligands, widely used as additives in lubricating oils,[3] is polymeric in the case of the ethyl derivative[1a] of the ligand whereas dimeric for the isopropyl derivative.[4] However, structure in solution phase was not studied in detailed in this system[4,5] although the monomer–dimer equilibrium has been studied extensively by variable-temperature ^{1}H NMR,[6] ^{31}P NMR,[7] and EPR[8] for several main

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[†] Metal Dialkyl Diselenophosphates. 10. For part 9, see ref 11i.

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group, transitional metal, and lanthanide compounds. We have observed from VT ^{31}P NMR spectra that ZnDDP exist as a monomer in solution at high temperature whereas it is a dimer at low temperature.

Although over the decades there has been a continuing interest in the transition metal complexes of dialkyl dithiphosphate ligands,[9] little attention has been given for the corresponding selenium analogue. Only few papers containing diselenophosphate ligands have been published where synthesis and spectroscopic properties of several transition metal complexes have been studied.[10] The first attempt toward the synthesis, characterization, and spectroscopic properties of Ag(I), Cu(I), Zn(II), Cd(II), Co(III), and Rh(III) complexes with diethyl diselenophosphate ligands was made by Zingaro and co-workers,[10a] but the structures were not well characterized either in the solid state or in the solution phase. Recently, several Cu(I) and Ag(I) compounds containing diselenophosphate ligands have been isolated and characterized[11] in our laboratory where most of the structures are completely different from the proposed structures by Zingaro. Besides, the unique properties of Se coordination require further studies as they possess both biological[12] and commercial importance.[13] Herein, we report the detailed synthesis, solid-state structures, and solution properties of $[Zn\{Se_2P(OEt)_2\}_2]_\infty$ (**1**) and $[Zn_2\{Se_2P(O^iPr)_2\}_4]$ (**2**). From ^{31}P NMR spectra at variable temperatures, it has been observed that both compounds are monomers in solution above 40 °C and dimers (or maybe a polymer in the case of compound **1**) below −90 °C in CD_2Cl_2.

Experimental Section

Materials and Measurements. All chemicals and reagents were purchased from commercial sources and used as received. Commercial CH_2Cl_2 and ROH were distilled from P_4O_{10} and Mg, respectively. Hexane and diethyl ether were distilled from Na/K. All the reactions were performed in oven-dried Schlenk glassware by using standard inert-atmosphere techniques. The ligand, $NH_4Se_2P(OR)_2$ (R = Et and ^{i}Pr),[10b,11e] and compounds $[Zn\{S_2P(OEt)_2\}_2]_\infty$ and $[Zn_2\{S_2P(O^iPr)_2\}_4]$ were prepared according to the literature methods.[5f] The elemental analyses were done using a Perkin-Elmer 2400 CHN analyzer. ^{1}H and ^{31}P NMR spectra were recorded on an Advance-300 Fourier transform spectrometers. ^{77}Se NMR spectra at 20 °C were done on a Bruker AC-F200 and at −30 °C were done on Bruker DMX-300 MHz. The $^{31}P\{^1H\}$ and $^{77}Se\{^1H\}$ NMR are referenced externally against 85% H_3PO_4 ($\delta = 0$) and PhSeSePh ($\delta = 463$), respectively. Positive FAB mass spectra were carried out on a VG 70-250S mass spectrometer with nitrobenzyl alcohol as the matrix.

Preparation of $[Zn\{Se_2P(OEt)_2\}_2]_\infty$ (1). $Zn(ClO_4)_2\cdot 6H_2O$ (2 mmol, 0.745 g) was dissolved in 20 mL of water in a 100 mL Schlenk flask. The water solution was deoxygenated by freeze−pump−thaw cycles method. This solution was then transferred by cannula to another 100 mL Schlenk flask containing diselenophosphate ligand [$NH_4Se_2P(OEt)_2$, 4 mmol, 1.188 g]. The solution mixture was stirred for 2 h at ambient temperature under nitrogen atmosphere. White precipitate was formed during the reaction period. The resulting white precipitate was filtered out and washed with ether. The white residue was then redissolved in dichloromethane and the solution layered with hexane, which afforded crystalline material of **1**. Yield: 60% (0.750 g). Anal. Calcd for

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Table 1. Selected Crystallographic Data for $[Zn\{Se_2P(OEt)_2\}_2]_\infty$ (**1**) and $[Zn_2\{Se_2P(O^iPr)_2\}_4]$ (**2**)

	1	**2**
formula	$C_8H_{20}O_4P_2Se_4Zn$	$C_{24}H_{56}O_8P_4Se_8Zn_2$
fw	623.39	1358.99
space group	$P2_1/n$	$C2/c$
a, Å	8.558(3)	11.239(8)
b, Å	19.803((7)	17.396(13)
c, Å	11.901(4)	25.915(13)
α, deg	90	90
β, deg	105.272(7)	99.46(5)
γ, deg	90	90
V, Å^3	1945.6(11)	4998(6)
Z	4	4
ρ_{calcd}, g cm^{-3}	2.128	1.806
λ(Mo Kα), Å	0.710 73	0.710 73
μ, mm^{-1}	8.913	6.948
T, K	298(2)	298(2)
R1[a]	0.0558	0.0669
wR2[b]	0.1396	0.1431

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

$C_8H_{20}ZnO_4P_2Se_4$: C, 15.40; H, 3.21. Found: C, 15.62; H, 3.35. FAB MS: m/z 968.8 ($Zn_2L_3^+$), 344.8 (ZnL^+). ^1H NMR ($CDCl_3$): δ 1.43 [t, 12H, OCH_2CH_3], 4.23 [m, 8H, OCH_2CH_3]. $^{31}P\{^1H\}$ NMR (20 °C, $CDCl_3$): δ 54.19 [br, 2P, $P(OEt)_2$, J_{PSe} = 567 Hz]. $^{77}Se\{^1H\}$ NMR (20 °C, $CDCl_3$): δ 226.8 [br, d, 4Se, $Se_2P(OEt)_2$, J_{SeP} = 566 Hz].

Preparation of $[Zn_2\{Se_2P(O^iPr)_2\}_4]$ (2). Compound **2** was prepared using a method similar to that described for complex **1**, except the white precipitate formed during the reaction period was redissolved in 10 mL of ether and slow evaporation of ether solution gave colorless crystals of **2**. Yield: 60% (0.816 g). Anal. Calcd for $C_{24}H_{56}Zn_2O_8P_4Se_8$: C, 21.19; H, 4.12. Found: C, 21.35; H, 4.16. FAB MS: m/z 1052.8 ($Zn_2L_3^+$). ^1H NMR ($CDCl_3$): δ 1.41 [d, 48H, $OCH(CH_3)_2$,], 4.87 [m, 8H, $OCH(CH_3)_2$]. $^{31}P\{^1H\}$ NMR (20 °C, $CDCl_3$): δ 46.4 [br, 4P, $P(O^iPr)_2$, J_{PSe} = 574 Hz]. $^{77}Se\{^1H\}$ NMR (20 °C, $CDCl_3$): δ 255.5 [br, 8Se, d, $Se_2P(O^iPr)_2$, J_{SeP} = 573 Hz].

Safety Note. *Perchlorate salts are potentially explosive! Selenium and its derivatives are toxic! These materials should be handled with great caution.*

X-ray Crystallographic Procedures. The structures of $[Zn\{Se_2P(OEt\ )_2\}_2]_\infty$ (**1**) and $[Zn_2\{Se_2P(O^iPr)_2\}_4]$ (2) were obtained by the single-crystal X-ray diffraction technique. Crystals were mounted on the tips of glass fibers with epoxy resin. Data were collected on a Siemens SMART CCD (charged coupled device) diffractometer. Cell parameters were retrieved with SMART software[14] and refined with SAINT software[15] on all observed reflection ($I > 10\sigma(I)$). Data reduction was performed with SAINT, which corrects for Lorentz and polarization effects. An empirical absorption correction was applied for **1** and **2**. The structures were solved by the use of direct methods, and refinement was performed by the least-squares methods on F^2 with the SHELXL-97 package,[16] incorporated in SHELXTL/PC V5.10.[17] Selected crystal data for the compounds (**1** and **2**) are summarized in Table 1.

Compound 1. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 layered with hexane. A colorless crystal (0.42 × 0.20 × 0.20 mm) was mounted, and data were collected. A total of 5906 reflections were collected, of which 3307 were unique (R_{int} = 0.0544) and 2426 were observed with $I > 2\sigma(I)$. H-atoms were added. The final cycle of the full-matrix least-squares refinement was based on 2426 observed reflections and 172 parameters and converged with unweighted and weighted agreement factors of R1 = 0.0558 and wR2 = 0.1396, respectively. The largest residual peak and hole are 1.020 and −0.719 e/Å^3.

Compound 2. Crystals suitable for X-ray diffraction were obtained by slow evaporation of hexane solution of the complex. A colorless crystal (0.40 × 0.20 × 0.10 mm) was mounted, and data were collected. A total of 8800 reflections were collected, of which 4151 were unique (R_{int} = 0.0582) and 2114 were observed with $I > 2\sigma(I)$. One of the isopropoxyl groups was found disordered. Bond distances were constrained. These constraints were O−C = 1.48 and 2.51 Å and C−C = 1.54 Å. H-atoms were added. The final cycle of the full-matrix least-squares refinement was based on 2114 observed reflections, 6 restraints, and 208 parameters and converged with unweighted and weighted agreement factors of R1 = 0.0669 and wR2 = 0.1431, respectively. The largest residual peak and hole are 0.622 and −0.426 e/Å^3.

Results and Discussion

Synthesis. The compounds $[Zn\{Se_2P(OEt)_2\}_2]_\infty$ (**1**) and $[Zn_2\{Se_2P(O^iPr)_2\}_4]$ (**2**) have been synthesized in ~60% yield from the reaction of $Zn(ClO_4)_2 \cdot 6H_2O$ and $(NH_4)[Se_2P(OR)_2]$ (R = Et and ^{i}Pr) in a molar ratio of 1:2 in deoxygenated water medium at room temperature. The compounds are also formed in methanol and ethanol but in lower yield. The yield of the isolated product is not high due to some other unidentified decomposition products. Elemental analyses of the compounds are in good agreement with the molecular formulation of **1** and **2**. Positive fast-atom bombardment mass spectra (FAB-MS) in nitrobenzyl alcohol show m/z peaks at 968.8 ($Zn_2L_3^+$) and 344.8 (ZnL^+) for **1** and 1052.8 ($Zn_2L_3^+$) for **2**. ^1H NMR spectra exhibit chemical shifts at δ 1.43 and 4.23 ppm for the $-CH_2CH_3$ group of dsep ligands in **1** and 1.41 and 4.87 ppm for the $-CH(CH_3)_2$ group of the dsep in **2**.

Structure of $[Zn\{Se_2P(OEt)_2\}_2]_\infty$ (1). Compound **1** is crystallized in the monoclinic space group $P2_1/n$ with 4 molecules/unit cell. A perspective view of compound **1** is shown in Figure 1, and selected bond distances and angles are given in Table 2. The molecular structure of the compound is a one-dimensional helical chain via bridging dsep ligands, and the structure is similar to its sulfur analogue, $[Zn\{S_2P(OEt)_2\}_2]_\infty$.[1a] All zinc atoms are connected by bridging dsep ligands with an additional chelating ligand at each zinc atom. Thus, dsep ligands exhibit a bimetallic biconnective (μ_2, η^2) and monometallic biconnective (η^2) coordination pattern. Each zinc atom is coordinated by four selenium atoms from two bridging and one chelating dsep ligands, and the geometry around zinc is basically distorted tetrahedral. The Zn···Zn distance is 7.147 Å, which is slightly longer than observed length, 6.821 Å, in $[Zn\{S_2P(OEt)_2\}_2]_\infty$. The Se···Se bite distances are 3.489 and 3.499 Å for bridging and chelating ligands, respectively, whereas the Se···Se bite distance in Cu^I clusters[11a,c,f] containing the bridging dsep ligand ranges from 3.700 to 3.811 Å and 3.637 to 3.778 Å

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(14) SMART V4.043: *Software for the CCD Detector System*; Bruker Analytical X-ray System: Madison, WI, 1995.

(15) SAINT V4.043: *Software for the CCD Detector System*; Bruker Analytical X-ray System: Madison, WI, 1995.

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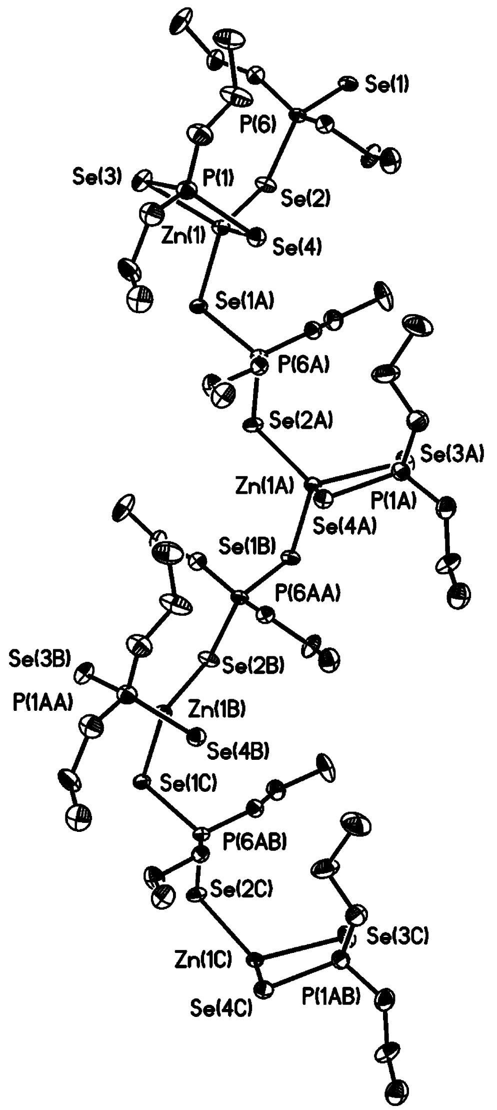

Figure 1. One-dimensional helical chain of $[Zn\{Se_2P(OEt)_2\}_2]_\infty$ (**1**) with atom-numbering scheme and thermal ellipsoids at the 50% probability level.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Zn\{Se_2P(OEt)_2\}_2]_\infty$ (**1**) with Esd's in Parentheses

Zn(1)−Se(2)	2.456(2)	Se(4)−Zn(1)−Se(3)	89.18(6)
Zn(1)−Se(1A)	2.468(2)	P(6)−Se(1)−Zn(1B)	99.54(7)
Zn(1)−Se(4)	2.470(2)	P(6)−Se(2)−Zn(1)	104.78(8)
Zn(1)−Se(3)	2.515(2)	P(1)−Se(3)−Zn(1)	80.20(9)
Se(1)−Zn(1B)	2.468(2)	P(1)−Se(4)−Zn(1)	81.42(9)
Se(1)−P(6)	2.150(3)	O(3)−P(1)−O(4)	95.1(5)
Se(2)−P(6)	2.153(2)	O(3)−P(1)−Se(4)	113.2(4)
Se(3)−P(1)	2.156(3)	O(4)−P(1)−Se(4)	112.4(4)
Se(4)−P(1)	2.147(3)	O(3)−P(1)−Se(3)	114.1(4)
P(1)−O(3)	1.572(8)	O(4)−P(1)−Se(3)	112.7(4)
P(1)−O(4)	1.584(9)	Se(4)−P(1)−Se(3)	108.83(13)
P(6)−O(1)	1.572(7)	Se(1)−P(6)−Se(2)	108.38(11)
P(6)−O(2)	1.575(7)	O(1)−P(6)−O(2)	97.4(4)
Se(2)−Zn(1)−Se(1A)	97.70(5)	O(1)−P(6)−Se(1)	112.4(3)
Se(2)−Zn(1)−Se(4)	124.16(6)	O(2)−P(6)−Se(1)	112.5(3)
Se(1A)−Zn(1)−Se(4)	117.55(6)	O(1)−P(6)−Se(2)	113.4(3)
Se(2)−Zn(1)−Se(3)	116.58(6)	O(2)−P(6)−Se(2)	112.5(3)
Se(1A)−Zn(1)−Se(3)	112.82(6)		

for Ag^I clusters.[11b,e] The Zn−Se distances lie between 2.456 Å and 2.514 Å, which are comparable with Zn−Se distances 2.462−2.481 Å in $[Me_4N]_2[Zn(SePh)_4]$[18] but longer, as expected, than the corresponding sulfur analogues which lie between 2.336 and 2.401 Å. The average P−Se distance is 2.152 Å, and the average P−O bond length is 1.576 Å. The Se−P−Se angles are 108.40 and 108.91° for bridging and chelating ligands, respectively, and 107.96 and 109.64° for the sulfur analogue, while the Se−P−Se angles lie in the range 116.20−124.20° for bridging dsep ligands in Cu^I and Ag^I clusters.[11] The Se−Zn−Se angles are 97.70 and 89.15° for bridging and chelating ligands, respectively, whereas they are 102.17 and 85.83° for the sulfur analogue, which indicates the geometry at the zinc center is appreciably distorted from tetrahedral.

Structure of $Zn_2\{Se_2P(O^iPr)_2\}_4]$ (2). Compound **2** is crystallized in the monoclinic space group *C*2/*c* with 4 molecules/unit cell. A perspective view of compound **2** is shown in Figure 2, and selected bond distances and angles are given in Table 3. The complex in the crystalline state exists as a dimer, similar to $[Zn_2\{S_2P(O^iPr)_2\}_4]$[4] and $[Zn_2\{Se_2CNEt_2\}_4]$[19] having a C_2 point group symmetry. The structure consists of two zinc atoms connected by two bridging dsep ligands, and each zinc atom is further chelated by a dsep ligand. Thus, an eight-membered ring in saddle-shape geometry was formed through two zinc atoms and two bridging dsep ligands. Both zinc atoms in a distorted tetrahedral geometry are coordinated by four selenium atoms from two bridging and one chelating dsep ligands. The Zn···Zn distance is 4.316 Å, which is longer than 3.77 Å in $[Zn_2\{Se_2CNEt_2\}_4]$ but comparable with 4.108 Å in $[Zn_2\{S_2P(O^iPr)_2\}_4]$. The Se···Se bite distances are 3.648 and 3.492 Å for bridging and chelating ligands, respectively, whereas the corresponding S···S bite distances are 3.355 and 3.231 Å in the sulfur analogue. Although Se···Se (or S···S) bite distances are almost equal for bridging and chelating ligands in the polymeric compounds, they are slightly longer in the case of the bridging ligand compared to the chelating ligand for dimeric compounds. The Zn−Se distances range between 2.422 and 2.524 Å, which are comparable to 2.435−2.568 Å in $Zn_2\{Se_2CNEt_2\}_4$. The average P−Se distances is 2.142 Å, and the average P−O bond length is 1.556 Å. The Se−P−Se angles are 117.17 and 108.85° for bridging and chelating ligands, respectively, and 117.31 and 109.70° for the sulfur analogue. The Se−Zn−Se angles are 122.78 and 88.85° for bridging and chelating ligands, and those for the sulfur analogue are 121.27 and 85.48°, respectively.

VT ^{31}P NMR Studies. Solution studies of both complexes were done at variable temperature ranging from +40 to −90 °C in CD_2Cl_2. Both of the complexes show similar patterns, and one representative spectrum for the complex $[Zn_2\{Se_2P(O^iPr)_2\}_4]$ (**2**) is shown in Figure 3. Therefore, the following discussion will concentrate on complex **2**. At normal NMR experimental temperature 20 °C, complex **2** exhibits a broad peak at δ 48.95 ppm, while with increasing temperature the broad peak gradually becomes sharp (Figure 3). At 40 °C, the peak becomes very sharp at δ 47.30 ppm with satellites (J_{PSe} = 573 Hz). This coupling constant is slightly larger

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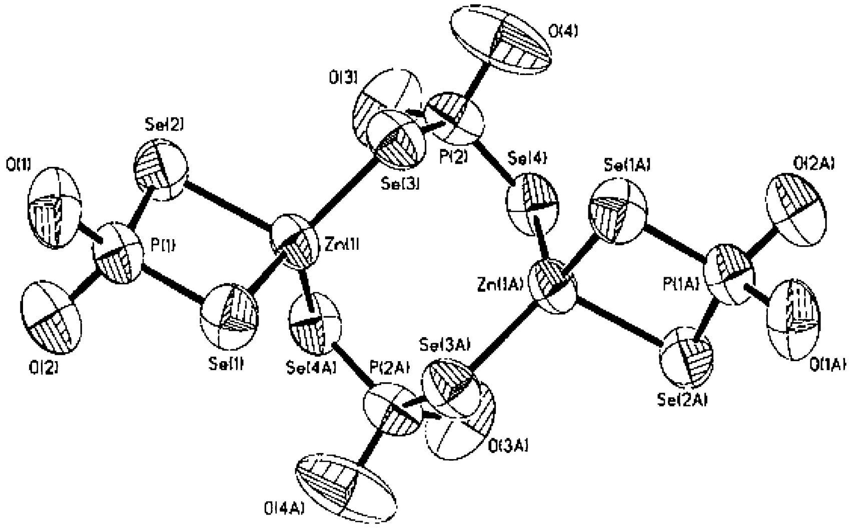

Figure 2. Thermal ellipsoid drawing (50% probability level) of [Zn$_2${Se$_2$P(O^{i}Pr)$_2$}$_4$] (**2**) with atom-numbering scheme. The isopropyl groups are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for [Zn$_2${Se$_2$P(O^{i}Pr)$_2$}$_4$] (**2**) with Esd's in Parentheses

Zn(1)−Se(4A)	2.422(2)	Se(1)−Zn(1)−Se(2)	88.85(6)
Zn(1)−Se(3)	2.425(2)	P(1)−Se(1)−Zn(1)	81.19(10)
Zn(1)−Se(1)	2.465(2)	P(1)−Se(2)−Zn(1)	80.05(11)
Zn(1)−Se(2)	2.524(2)	P(2)−Se(3)−Zn(1)	102.86(11)
Se(4)−Zn(1A)	2.422(2)	P(2)−Se(4)−Zn(1A)	98.80(11)
Se(1)−P(1)	2.153(4)	O(2)−P(1)−O(1)	95.8(5)
Se(2)−P(1)	2.141(4)	O(2)−P(1)−Se(2)	112.8(4)
Se(3)−P(2)	2.138(4)	O(1)−P(1)−Se(2)	113.4(4)
Se(4)−P(2)	2.135(4)	O(2)−P(1)−Se(1)	112.9(4)
P(1)−O(2)	1.559(8)	O(1)−P(1)−Se(1)	112.8(4)
P(1)−O(1)	1.569(9)	Se(2)−P(1)−Se(1)	108.85(15)
P(2)−O(4)	1.532(11)	Se(4)−P(2)−Se(3)	117.22(15)
P(2)−O(3)	1.564(12)	O(4)−P(2)−O(3)	108.6(8)
Se(4A)−Zn(1)−Se(3)	122.80(7)	O(4)−P(2)−Se(4)	105.6(6)
Se(4A)−Zn(1)−Se(1)	114.50(9)	O(3)−P(2)−Se(4)	110.5(5)
Se(3)−Zn(1)−Se(1)	109.79(8)	O(4)−P(2)−Se(3)	108.9(5)
Se(4A)−Zn(1)−Se(2)	106.61(7)	O(3)−P(2)−Se(3)	105.8(5)
Se(3)−Zn(1)−Se(2)	108.65(8)		

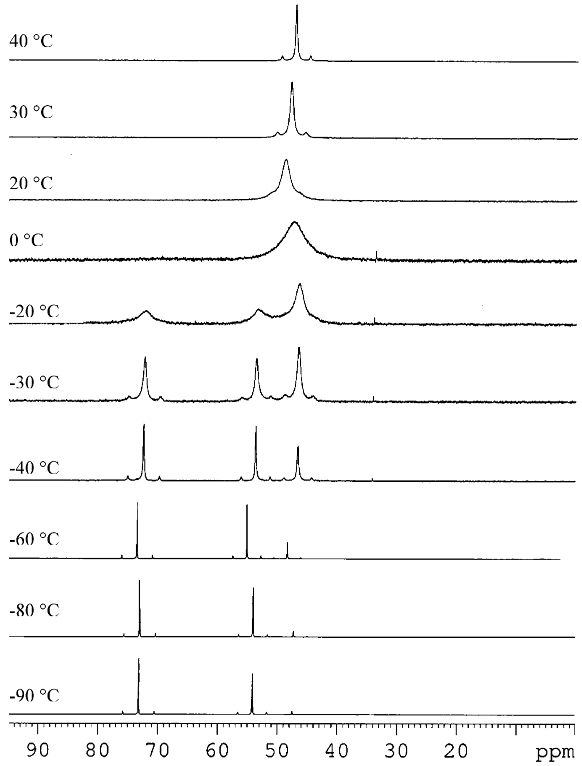

Figure 3. Variable-temperature ^{31}P NMR spectra of [Zn$_2${Se$_2$P(O^{i}Pr)$_2$}$_4$].

than ^1J(PSe) = 539 Hz in the compound Zn[N(SeP^{i}Pr$_2$)$_2$]$_2$,[20] a mononuclear zinc tetrahedrally coordinated by four selenium atoms.

As the temperature is lowered, the peak becomes broad and most broadening takes place at 0 °C at ~47.39 ppm, while, at −20 °C, two new broad peaks appear and are centered at δ 72.22 and 53.38 ppm with the original broad peak at δ 46.46 ppm. At −40 °C all three broad peaks become sharp peaks at δ 46.74, 53.78, and 72.55 ppm with satellites (J_{PSe} = 573, 587, 640 Hz, respectively). With further decrease of temperature to −60 and −80 °C, the peak intensity at δ 46.74 ppm gradually decreases, while the other two peaks intensities (δ 53.78 and 72.55 ppm) increase slightly and they are equal in intensity. At −90 °C the peak at δ 46.74 ppm becomes almost negligible (0.01%) compared to other two peaks (δ 53.78 and 72.55 ppm), which are equal in intensity from the integration value although one is looking a little smaller. This is a very important observation which has not been studied earlier by variable-temperature ^{31}P NMR for the analogous sulfur compounds, [Zn{S$_2$P(OEt)$_2$}$_2$]$_\infty$ or [Zn$_2${S$_2$P(O^{i}Pr)$_2$}$_4$], although association studies[5d] have shown that monomers are in equilibrium with dimers in the isopropyl derivative. We have also studied VT ^{31}P NMR for [Zn{S$_2$P(OEt)$_2$}$_2$]$_\infty$ and [Zn$_2${S$_2$P(O^{i}Pr)$_2$}$_4$] and obtained similar results. From these observations it is clear that the monomer and dimer (Scheme 1) of the complex are in equilibrium in solution at 20 °C. At temperatures above 40 °C, the complex exists as a monomer and shows a very sharp peak. As the temperature is reduced, the percentage of dimer increases gradually at the expense of monomer. Below −90 °C the complex exists as a dimer, and two peaks (δ 72.55 and 53.78 ppm) with equal intensities are due to bridging

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Scheme 1. Monomer and Dimer in Equilibrium in Solution

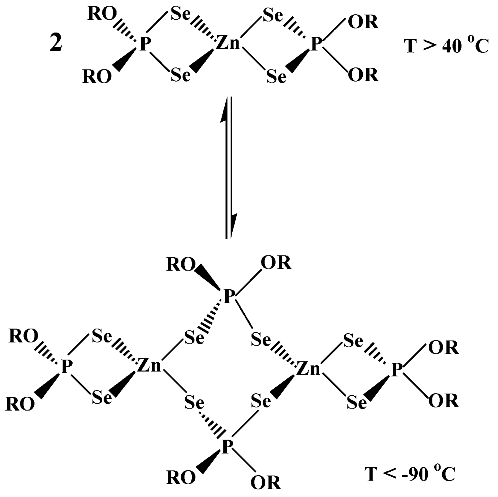

Table 4. Equilibrium Constant for **1** and **2** at Various Temperatures

T, K	K_{eq}, L/mol, of **1** (CD_2Cl_2)	K_{eq}, L/mol, of **2** (CD_2Cl_2)	K_{eq}, L/mol, of **1** ($CDCl_3$)	K_{eq}, L/mol, of **2** ($CDCl_3$)
240.1	2.2	1.3	1.7	0.15
235	3.9	1.9	2.4	0.35
228.4	6.5	3.5	4.1	0.61
219.4	22.7	8.9	7.2	1.2
215.3	38.2	13.8	9.1	1.6
205.6	66.3	75.8		
200	96.4	109.6		

and chelating ligands, respectively. However, in the case of complex **1** which is a polymer in the solid state, the possibility of existence of a polymer below −90 °C cannot be ruled out completely as two peaks (δ 78.41 and 58.66 ppm) may be also due to bridging and chelating ligands, respectively, in the polymeric structure. From VT ^{31}P NMR of the compounds **1** and **2** in $CDCl_3$ and CD_3COCD_3, it has been found that the monomer−dimer equilibrium is also solvent dependent as we obtained different ratios of monomer and dimer at the same temperature. Equilibrium constants (K_{eq}) for the monomer−dimer equilibrium were obtained from the concentrations of monomeric and dimeric species calculated from the ^{31}P NMR spectra by careful intergration at various temperatures, and some of them are given in Table 4. Van't Hoff analysis[21] of these data for dimerization of two monomeric species gave $\Delta H = -33.6 \pm 0.8$ kJ mol^{-1} and $\Delta S = -10.5 \pm 0.4$ J K^{-1} mol^{-1} for compound **1** and $\Delta H = -43 \pm 0.8$ kJ mol^{-1} and $\Delta S = -3 \pm 0.4$ J K^{-1} mol^{-1} for **2**. The bridging and chelating ligands undergo dynamic exchange (Scheme 1) for which the free energy of activation is calculated from the coalescence temperature[22] as $\Delta G^{\ddagger}_{(273K)} =$ 45.0 kJ mol^{-1} for **1** and $\Delta G^{\ddagger}_{(273K)} = 44.09$ kJ mol^{-1} for **2**.

We have also recorded the ^{77}Se NMR spectra in $CDCl_3$ at −30 °C for both complexes. Compound **1** exhibits three doublets at δ 254, 237.4, and 92.9 ppm whereas compound **2** shows at δ 254, 237, and 94 ppm. The doublet at δ 254 is due to the presence of a monomer, and the other two doublets, which are equal in intensity, are due to the presence of a dimer in solution. Variable-temperature ^{1}H NMR is not informative as peaks are sharp at normal temperature and almost unchanged with variation of temperature.

Conclusion

Two zinc complexes containing dialkyl diselenophosphate ligands have been synthesized. The solid-state structure of complex **1** is a polymer via symmetrically bridging dsep ligands, while complex **2** is a dimer in the crystalline state possibly due to steric requirments. Each zinc atom is connected by four selenium atoms in a tetrahedral geometry from two bridging dsep ligands with an additional chelating ligand. However, variable-temperature ^{31}P NMR studies suggested a monomer−dimer equilibrium in solution via exchange bridging and chelating ligands. Thus, at temperatures above 40 °C, the complexes exists as monomers, whereas dimers are favored at lower temperatures and below −90 °C the complexes exists as dimers (or a polymer in the case of **1**).

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Supporting Information Available: X-ray crystallographic files in CIF format for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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