



Nonaqueous synthesis of molecular zinc amide phosphate

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ABSTRACT

Three new molecular zinc compounds were prepared by nonaqueous reactions of $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ and ZnEt_2 with trimethylsilylestere of phosphoric acid, $\text{OP}(\text{OSiMe}_3)_3$ and $\text{OP}(\text{OSiMe}_3)_2(\text{OH})$. Single-crystal X-ray diffraction analyses of crystalline products revealed molecular structures of two mononuclear complexes $[\text{ZnX}_2\text{OP}(\text{OSiMe}_3)_3]$ ($\text{X} = \text{N}(\text{SiMe}_3)_2$ (**1**), $\text{hfacac} = \text{hexafluoroacetylacetonate}$, (**2**)) and one dinuclear zinc phosphate $[(\text{Zn}\{\{\text{py}\}\text{N}(\text{SiMe}_3)_2\}\{\mu_2\text{-O}_2\text{P}(\text{OSiMe}_3)_2\})_2]$ (**3**). Compound **1** is only the second structurally characterized adduct of zinc bisamide with an oxygen donor and a three-coordinate Zn atom. The cyclic inorganic core $\{\text{Zn}(\mu_2\text{-O}_2\text{PO}_2)\}_2$ in **3** is a model for the most common single four-ring (S4R) building unit of open-framework zinc phosphates. The molecule of **3** possesses reactive amide and trimethylsilyloxy groups that can be employed in further studies on the formation of extended structures by condensation reactions. Spectroscopic properties and thermal behavior of the molecular products were examined. Compounds **1** and **3** were converted to $\alpha\text{-Zn}_2\text{P}_2\text{O}_7$ by calcination.

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1. Introduction

Zinc phosphates [1–5] and phosphonates [6–8] constitute a very rich and structurally interesting group of compounds that include species featuring various nuclearity, dimensionality and architecture modes. The unabated interest in these compounds spans from their function as open-framework materials to their use as seeds for spatial control of nucleation and growth of metal-organic framework (MOF) nanostructures [9] to models in nanoparticle composition and homogeneity studies by MAS NMR [10]. Open-framework zinc phosphates are studied for their potential applications in catalysis, sorption, ion exchange, and luminescence [11]. The most pertinent for these purposes are 3-dimensional (3D) zeolite-like networks [12–16] but layer (2D) [17–20] and chain or ladder (1D) [21,22] structures are also frequently reported. The mechanism of formation of zinc phosphates was investigated with considerable effort and it was shown that low dimensional structures can be converted to higher-dimensionality frameworks upon changing reaction conditions [23–25]. Analysis of these reactions suggests that small clusters serve as the starting species that condense to chains or ladders and subsequently transform to layer structures to finally form 3D frameworks [26,27]. The major synthetic route to zinc phosphates is the hydrothermal synthesis employing zinc salts, phosphoric acid and organic amines serving

as the templates. Additionally, the amine phosphate method [23] and nonaqueous routes with organophosphorous precursors, such as esters [28] and amides [29], were devised. The molecular zinc phosphates and phosphonates have been mainly prepared by the reactions of zinc precursors, such as ZnR_2 ($\text{R} = \text{Me}, \text{Et}$), $\text{Zn}(\text{OAc})_2$, ZnCl_2 , ZnO , with phosphoric and phosphonic acids and their alkyl and aryl esters and feature a variety of cage structures [30–33]. The reactions often involve bases with O and N donor atoms which are then included as co-ligands in the coordination spheres of zinc atoms or compensate the cluster charge as protonated cations. One of the frequent structural motifs is a cube-like double-four-ring (D4R) unit that was used for the assembly of zinc phosphates with different supramolecular architectures [34–38]. By far the most prevalent molecular units in zinc phosphates are $\text{Zn}_2\text{P}_2\text{O}_4$ cycles, also called single-four-rings (S4R) [39–41], which were shown to be important intermediates in the formation of open-framework structures. These basic units are formed as the first oligomers in the reaction process and are also the most common structural motifs in the crystalline higher-dimensional structures where they become connected to chains, ladders, layers or 3D-networks [42–45]. The molecular zinc phosphates were also used directly as precursors in the thermolytic preparation of layer and ceramic materials [46–48].

Nonaqueous or organometallic synthetic routes to oxide and phosphate materials offer certain advantages over their aqueous counterparts, such as a better control of condensation reactions, residual reactive functional surface groups in products, and a wider choice of precursors. These nonaqueous condensation reactions

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provided a large number of molecular and extended-structure metal phosphates and phosphonates. The reactions of metal amides or metal alkyls with tris(trimethylsilyl)ester of phosphoric acid [49,50] are based on silylamide or alkylsilane elimination or treatment of metal alkyls with phosphonic acids [51–53] can be employed.

Here we report results of our study focused on the nonaqueous synthesis of molecular zinc phosphates employing reactions of two trimethylsilylestere of phosphoric acid, OP(OSiMe₃)₃ and OP(OSiMe₃)₂(OH), with Zn[N(SiMe₃)₂]₂ and/or ZnEt₂. 1,1,1,5,5,5-hexafluoropentan-2,4-dione (hexafluoroacetylacetone, Hhfacac) was used in a subsequent reaction with bis(trimethylsilyl)amine groups and modified the Zn coordination sphere. Thermal treatment was employed to convert molecular products to α -Zn₂P₂O₇.

2. Experimental section

2.1. General methods

All manipulations were performed in a dry nitrogen atmosphere using combined Schlenk and Stock techniques as well as in an M. Braun drybox with both H₂O and O₂ levels below 1 ppm. Zn [N(SiMe₃)₂]₂ was synthesized from ZnCl₂ and LiN(SiMe₃)₂ according to literature [54,55]. OP(OSiMe₃)₃ was prepared from H₃PO₄ and Me₃SiCl [56] and vacuum-distilled. OP(OSiMe₃)₂(OH) was prepared by the reaction of KH₂PO₄ with Me₃SiCl [57]. ZnEt₂ (1 M solution in heptane) and Hhfacac (1,1,1,5,5,5-hexafluoropentan-2,4-dione) were purchased from Aldrich and used as received. Toluene and hexane were freshly distilled from Na/benzophenone under N₂; pyridine was predried over KOH and distilled from phosphorus pentoxide before use. Benzene-*d*₆ was dried over and distilled from Na/K alloy and degassed prior to use. CDCl₃ was dried by P₂O₅ and vacuum-transferred to an ampoule.

2.2. Characterization

The IR spectra (4000–400 cm⁻¹) were recorded on a Bruker Tensor T27 spectrometer. Samples were prepared as KBr pellets.

CHN elemental analyses were performed at the Institute of Chemistry, UNAM, Mexico. Thermal analysis (TG/DSC) was measured on a Netzsch STA 449C Jupiter apparatus from 25 to 1100 °C under flowing air (70 cm³ min⁻¹) with a heating rate of 5 K min⁻¹. The Zn and P content was analyzed on an ICP-OES spectrometer Jobin Yvon 170 Ultrace (generator 40 MHz, amplitude 1.0 kW, plasma gas flow 12 dm³ min⁻¹) with the use of absorption lines 213.618 nm (P) and 202.548 nm (Zn). The solution NMR spectra were recorded on a Bruker Avance II 300 NMR spectrometer at frequencies 300.1 MHz for ¹H, 75.5 MHz for ¹³C, 282.4 MHz for ¹⁹F, 121.5 MHz for ³¹P, 59.6 MHz for ²⁹Si with deuterated solvents as the external lock. The ¹H and ¹³C{¹H} NMR spectra were referenced to the residual proton signals or carbon resonances of benzene-*d*₆ (7.16 and 128.39 ppm, respectively) and CDCl₃ (7.24 and 77.23 ppm, respectively). EI-MS spectra were obtained on TSQ Quantum XLS with use of direct insertion probe method. The ionization energy was set to 10 eV and the spectra were scanned for *m/z* 35–1100 Da. APCI-MS measurement was performed on Agilent 6224 TOF LC-MS system. Solid samples were dissolved in toluene. The samples were injected via syringe pump KDS Model 100 Series (KD Scientific, Inc., USA) into the electrospray ion source at a flow rate of 30 μ l min⁻¹ for two minute long analyses. The spectra were recorded both in positive and negative mode for *m/z* 30–3200 Da at 4 GHz tuning for high resolution instrument mode. The drying gas temperature of 200 °C and the drying gas flow of 7 l/min with 30 psig for the nebulizer pressure were used for ionization of analytes in ion source/ESI. The fragmentor was set to 10 V and the capillary voltage was –2000/4000 V (+/–APCI). A Stoe-Cie transmission diffractometer STADI P operating with a Ge monochromatized Co (1.788965 Å) radiation (40 kV, 30 mA) and equipped with a PSD detector was used for the XRD data acquisition at ambient temperature.

Diffraction data were collected on a KUMA KM-4 κ -axis CCD diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å). The temperature during data collection was 120(2) K. The structures were solved by direct methods and refined by standard methods using ShelXTL software package [58]. Details of the data collection and structure refinement are listed in Table 1.

Table 1
Crystal data and structure refinement parameters.

Compound number	1	2	3
Empirical formula	C ₂₁ H ₆₃ N ₂ O ₄ PSi ₇ Zn	C ₁₉ H ₂₉ F ₁₂ O ₈ PSi ₃ Zn	C ₁₇ H ₄₁ N ₂ O ₄ PSi ₄ Zn
fw	700.70	794.03	546.22
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	<i>Pbca</i>	<i>P1</i>	<i>P2₁/n</i>
Temperature, K	120(2)	120(2)	120(2)
λ , Å	0.71073	0.71073	0.71073
<i>a</i> , Å	22.0917(6)	10.7368(10)	12.3954(17)
<i>b</i> , Å	21.6835(4)	11.2924(9)	13.265(4)
<i>c</i> , Å	17.4249(4)	15.5880(14)	17.876(7)
α , deg	90	76.262(7)	90
β , deg	90	87.483(7)	100.458(18)
γ , deg	90	71.926(7)	90
<i>V</i> , Å ³	8347.0(3)	1744.4(3)	2890.4(15)
<i>Z</i>	8	2	4
μ , mm ⁻¹	0.852	0.953	1.093
No. of reflns collected	92,270	18,616	18,662
No. of indep. reflns (<i>R</i> _{int})	7347 (0.0573)	6112 (0.0170)	5090 (0.0231)
No. of data/restraints/parameters	7347/33/398	6112/0/406	5090/0/274
GoF on <i>F</i> ²	1.207	0.884	1.069
<i>R</i> ₁ ^a <i>wR</i> ₂ ^b (<i>I</i> > 2 σ (<i>I</i>))	0.0424, 0.0948	0.0387, 0.1106	0.0356, 0.0912
<i>R</i> ₁ ^a <i>wR</i> ₂ ^b (all data)	0.0698, 0.1191	0.0561, 0.1332	0.0626, 0.1194
Largest diff. peak/hole, e Å ⁻³	0.731/–0.622	0.808/–0.551	0.632/–0.351

^a $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$.

^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum (F_o^2)^2]^{1/2}$.

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