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Molecular Indium(III) Phosphonates Possessing Ring and Cage Structures. Synthesis and Structural Characterization of $[In_2(t\text{-}BuPO_3H)_4(phen)_2Cl_2]$ and $[In_3(C_5H_9PO_3)_2(C_5H_9PO_3H)_4(phen)_3]\cdot NO_3\cdot 3.5H_2O$

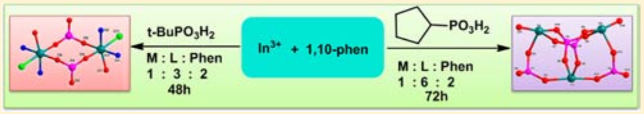
Vadapalli Chandrasekhar,*[†,‡] Joydeb Goura,[†] and Andrew Duthie[§]

[†]Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016, India

[‡]Centre for Interdisciplinary Sciences, Tata Institute of Fundamental Research, 21 Brundavan Colony, Narsingi, Hyderabad 500075, India

[§]School of Life and Environmental Sciences, Deakin University, Geelong 3217, Australia

Supporting Information

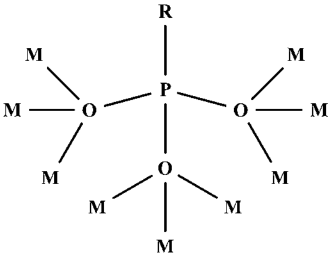


ABSTRACT: Two novel indium(III) phosphonates, $[In_2(t\text{-}BuPO_3H)_4(phen)_2Cl_2]$ (**1**) and $[In_3(C_5H_9PO_3)_2(C_5H_9PO_3H)_4(phen)_3]\cdot NO_3\cdot 3.5H_2O$ (**2**) with phen = 1,10-phenanthroline, have been synthesized by solvothermal reactions involving indium(III) salts and organophosphonic acids. **1** is a dinuclear compound where the two indium centers are bridged by a pair of isobidentate phosphonate ligands, $[t\text{-}BuP(O)_2OH]^-$, resulting in an eight-membered $(In_2P_2O_4)$ puckered ring. Compound **2** is trinuclear; the In_3 platform is held together by two bicapping tripodal phosphonate ligands from the top and bottom of the indium plane. In addition, two bridging monoanionic phosphonate ligands serve to bind two pairs of indium centers. Both **1** and **2** also contain monodentate monoanionic phosphonate ligands. The solid-state MAS ^{31}P NMR spectrum of complex **1** shows two signals at 21.9 and 29.3 ppm. Compound **2** contains signal maxima at 25.8 and 28.9 ppm, with a shoulder at 31.5 ppm. Room temperature solid-state fluorescence spectra of **1** and **2** are characterized by strong emission bands at 385 nm (λ_{ex} = 350 nm) and 395 nm (λ_{ex} = 350 nm), respectively, which are red-shifted with respect to the emission of free phenanthroline.

INTRODUCTION

There has been considerable research interest in recent years on the use of organophosphonates, $[RPO_3]^{2-}$, and related ligands such as $[RP(OH)O_2]^-$.[1] This interest arises mainly because of the versatile coordination capability of these multisite coordinating ligands. For example, a single $[RPO_3]^{2-}$ ligand potentially can bind up to nine metal centers (Chart 1). Even though this full potential is rarely realized, several instances of multisite coordination are known with phosphonate ligands.[1] In fact, such a propensity to bind to metal ions often leads to the formation of insoluble compounds that possess extended structures.[1] Many such compounds have been extensively studied because of their applications in a variety of fields such as catalysis, ion-exchange materials, sensors, etc.[2−4] The possibility of realizing molecular compounds with phosphonate ligands has been intriguing chemists for several years now, and various strategies have been designed to achieve this goal.[1] These include the use of ancillary ligands that limit the number of available coordination sites on the metal ion as well as the use of sterically hindered phosphonic acids.[5] A number of discrete molecular transition-metal phosphonates of varying nuclearity have now been prepared using these approaches.[6−9] However, among the main-group metal phosphonates, there is still a considerable amount of work that needs to be done. The reactions of organotin oxides/hydroxides/oxide−hydroxides with phosphonic/phosphinic acids have proven to be a rich mine of extremely novel compounds with a tremendous amount of structural diversity.[10] It is quite likely that such possibilities also exist with other main-group metals. Some investigations on aluminum, gallium, and boron phosphonates are known.[11−13] In the case of indium, some phosphates,[14] phosphites,[15] and phosphate−phosphites[15] are known. These possess pillared,[16] lamellar,[17] or open-framework structures,[18] as shown in many instances by powder X-ray diffraction (PXRD) studies.

Chart 1. Coordination Capability of a $[RPO_3]^{2-}$ Ligand



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Richards and co-workers recently reported the first single-crystal X-ray structure of an indium(III) phosphonate that possessed an extended structure.[19] Thus far, there are no examples of discrete molecular indium(III) phosphonates. Herein, we report the synthesis, crystal structures, solid-state ^{31}P NMR, solid-state fluorescence, and thermal analysis of two molecular indium(III) phosphonates, $[In_2(t\text{-}BuPO_3H)_4(phen)_2Cl_2]$ (**1**) and $[In_3(C_5H_9PO_3)_2(C_5H_9PO_3H)_4(phen)_3]\cdot NO_3\cdot 3.5H_2O$ (**2**) where phen = 1,10-phenanthroline, which possess a ring and a cage structure, respectively.

■ EXPERIMENTAL SECTION

Reagents and General Procedures. High-purity $InCl_3$ (anhydrous), $In(NO_3)_3\cdot 5H_2O$, C_5H_9Cl, and 1,10-phenanthroline were purchased from Aldrich Chemical Co. (Milwaukee, WI). $AlCl_3$, PCl_3, and *tert*-butyl chloride (S. D. Fine Chemicals, India) were used as received. Solvents and other general reagents used in this work were purified according to standard procedures.[20] *tert*-Butylphosphonic acid ($t\text{-}BuPO_3H_2$) and cyclopentylphosphonic acid ($C_5H_9PO_3H_2$) were prepared according to published procedures.[21]

Instrumentation. ^{1}H and ^{31}P NMR were recorded in $CDCl_3$ solutions using a JEOL-JNM Lambda 400 model NMR spectrometer operating at 400.0 and 161.7 MHz, respectively. Chemical shifts are referenced to tetramethylsilane. Solid-state magic-angle-spinning (MAS) ^{31}P NMR was measured at 161.83 MHz using a JEOL Eclipse Plus 400 spectrometer equipped with a 6 mm rotor operating at spinning frequencies of 8−10 kHz. Crystalline $NH_4H_2PO_4$ (δ 0.95) was used as the secondary reference. IR spectra were recorded as KBr pellets on a Bruker Vector 22 FT IR spectrophotometer operating from 400 to 4000 cm^{-1}. Elemental analyses of the compounds were obtained using a Thermoquest CE instrument CHNS-O, EA/110 model. Thermogravimetric analysis (TGA; heating rate of 10 °C/min) was carried out on a Perkin-Elmer Pyris 6 machine under an argon atmosphere. Solid-state emission spectra were recorded on a Perkin-Elmer-Lambda 20 spectrophotometer.

Synthesis. *$[In_2(t\text{-}BuPO_3H)_4(phen)_2Cl_2]$ (1).* A methanolic (5 mL) solution of 1,10-phenanathroline (0.148 g, 0.822 mmol) was gently poured into an aqueous solution (10 mL) of indium(III) chloride (0.091 g, 0.411 mmol). A methanolic solution (5 mL) of *tert*-butylphosphonic acid (0.170 g, 1.231 mmol) was added dropwise to this reaction mixture with constant stirring for 15 min at room temperature. The resultant reaction mixture was transferred into a Teflon-lined stainless steel autoclave and heated under autogenous pressure at 160 °C for 2 days. Overnight cooling of the vessel to room temperature resulted in colorless block-shaped crystals that were washed with diethyl ether and dried. Yield: 0.125 g, ~50% (based on indium). Mp: >220 °C. Anal. Calcd for $C_{40}H_{56}Cl_2In_2N_4O_{12}P_4$ (1209.31, **1**): C, 39.73; H, 4.67; N, 4.63. Found: C, 39.77; H, 4.70; N, 4.68. IR (KBr, ν, cm^{-1}): 3755(m), 3424(w), 3078(m), 2869(s), 2297(w), 1628(s), 1588(s), 1524(s), 1477(s), 1433(s), 1360(s), 1241(s), 1180(s), 1109(s), 1050(s), 931(s), 864(s), 790(m), 729(s), 652(s), 496(s), 421(s). ^{31}P NMR: δ 21.9 and 29.3

$[In_3(C_5H_9PO_3)_2(C_5H_9PO_3H)_4(phen)_3]\cdot NO_3\cdot 3.5H_2O$ (2). A methanolic (5 mL) solution of 1,10-phenanthroline (0.118 g, 0.655 mmol) was gently poured into an aqueous solution (10 mL) of $In(NO_3)_3\cdot 5H_2O$ (0.128 g, 0.327 mmol). A methanolic solution (5 mL) of cyclopentylphosphonic acid (0.295 g, 1.965 mmol) was added dropwise to this reaction mixture and stirred for 15 min at room temperature. The resultant reaction mixture was transferred into a Teflon-lined stainless steel autoclave and heated under autogenous pressure at 160 °C for 3 days. Overnight cooling of the vessel to room temperature resulted in colorless block-shaped crystals that were washed with diethyl ether and dried. Yield: 0.123 g, 64% (based on indium). Mp: >235 °C. Anal. Calcd for $C_{66}H_{89}In_3N_7O_{24.5}P_6$ (1902.73, **2**): C, 41.66; H, 4.71; N, 5.15. Found: C, 41.74; H, 4.75; N, 5.21. IR (KBr, ν, cm^{-1}): 3445(w), 3065(w), 2951(s), 2865(s), 1624(m), 1585(m), 1520(s), 1495(s), 1451(s), 1431(s), 1384(s), 1328(s), 1162(m), 1105(m), 1078(m), 1016(m), 8684(s), 855(s), 726(s), 647(s), 562(s), 496(s), 424(s). ^{31}P NMR: δ 25.8 and 28.9, shoulder at δ 31.5. A signal at δ 20.1 is also seen with very low intensity.

X-ray Crystallography. Single-crystal X-ray structural studies of **1** and **2** were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected using graphite-monochromated Mo Kα radiation (λ_α = 0.71073 Å). Crystals did not degrade/decompose during data collection. Data collection, structure solution, and refinement were performed using *SMART*, *SAINT*, and *SHELXTL* programs, respectively.[22a−f] All calculations for data reduction were done using the Bruker *SADABS* program. All non-hydrogen atoms were refined anisotropically using full-matrix least-squares procedures. All hydrogen atoms were included in idealized positions using a riding model. All mean-plane analyses and molecular drawings were obtained from *DIAMOND* (version 3.1).

■ RESULTS AND DISCUSSION

In the present contribution, we have used solvothermal reaction conditions and found that the combination of indium(III) salts [$InCl_3$ or $In(NO_3)_3\cdot 5H_2O$], organophosphonic acids (cyclopentylphosphonic acid and *tert*-butylphosphonic acid), and chelating nitrogen ligands (1,10-phenanthroline) afforded molecular di- and trinuclear ensembles **1** and **2**, respectively.

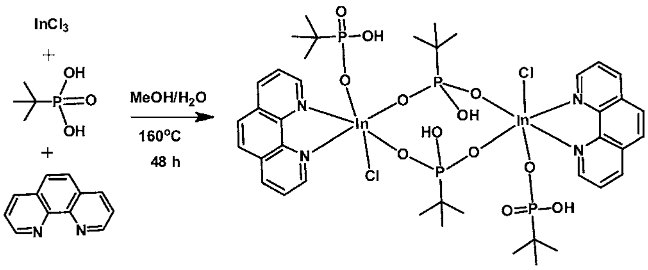
The molecular structures of **1** and **2** were determined by X-ray crystallography, with both complexes crystallizing in the monoclinic crystal system. The crystallographic parameters of these compounds are given in Table 1.

Table 1. Crystal Data and Structure Refinement Parameters of 1 and 2

	1	**2**
formula	$C_{40}H_{56}Cl_2In_2N_4O_{12}P_4$	$C_{132}H_{178}In_6N_{14}O_{49}P_{12}$
fw	1209.31	3805.46
temp (K)	100(2)	100(2)
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
unit cell dimens		
a (Å)	12.1925(18)	17.854(5)
b (Å)	10.6948(16)	40.106(5)
c (Å)	19.8070(3)	21.363(5)
α (deg)	90	90
β (deg)	105.909(2)	94.303(5)
γ (deg)	90	90
volume (Å^3), Z	2483.8(6), 2	15254(6), 4
density (Mg m^{-3})	1.617	1.657
abs coeff (mm^{-1})	1.225	1.106
F(000)	1224	7736
cryst size (mm^3)	0.14 × 0.12 × 0.11	0.14 × 0.12 × 0.09
θ range (deg)	2.18−26.00	1.90−25.50
limiting indices	$-15 \leq h \leq 13$	$-16 \leq h \leq 21$
	$-13 \leq k \leq 9$	$-48 \leq k \leq 48$
	$-23 \leq l \leq 24$	$-22 \leq l \leq 25$
reflns collected	13455	83100
unique reflns [R_{int}]	4861 [0.0548]	28355 [0.1176]
completeness to θ (%)	99.6 (26.00°)	99.8 (25.50°)
data/restraints/param	4861/0/300	28355/14/1806
GOF on F^2	1.145	1.011
final R indices [$I > 2\sigma(I)$]	R1 = 0.0421, wR2 = 0.1002	R1 = 0.0880, wR2 = 0.1993
R indices (all data)	R1 = 0.0616, wR2 = 0.1341	R1 = 0.1735, wR2 = 0.2520
largest diff peak/hole (e Å^{-3})	1.179/−0.804	1.528/−0.780

Complex **1** is dinuclear, where the two indium centers are bridged by isobidentate phosphinate ligands, [*t*-BuP(O)$_2$OH]$^-$, resulting in an eight-membered (In$_2$P$_2$O$_4$) puckered ring (see Scheme 1, Figure 1, and the Supporting Information). Such structural motifs are known in other instances: [Mn$_2$(*t*-BuPO$_3$H)$_4$(phen)$_2$]·2DMF where phen = 1,10-phenanthroline,[23] [Mn$_2$(*m*-HO$_3$SC$_6$H$_4$PO$_3$H$_2$)$_2$(phen)$_4$],[24] [Cu$_2$(μ_2-C$_5$H$_9$PO$_3$)$_2$(bpya)$_2$(H$_2$O)$_2$](H$_2$O)$_4$)[8a] where bpya = 2,2-bipyridylamine, and [Cd$_2$(ArPO$_3$H)$_4$(bpy)$_2$](CH$_3$OH)(H$_2$O)[25] where bpy = 2,2-bipyridine. While **1** and **2** represent direct synthesis of indium(III) phosphonates, it may be mentioned that hydrolysis of (Me$_2$InPPh$_2$)$_2$ has been reported to afford an organoindium derivative, [InMe(OH)(O$_2$PPh$_2$)]$_4$·(py)$_4$. In the latter, each phosphinate ligand binds two adjacent indium centers, while additionally three indium centers are bridged by a μ_3-OH.[26]

Scheme 1. Synthesis of 1



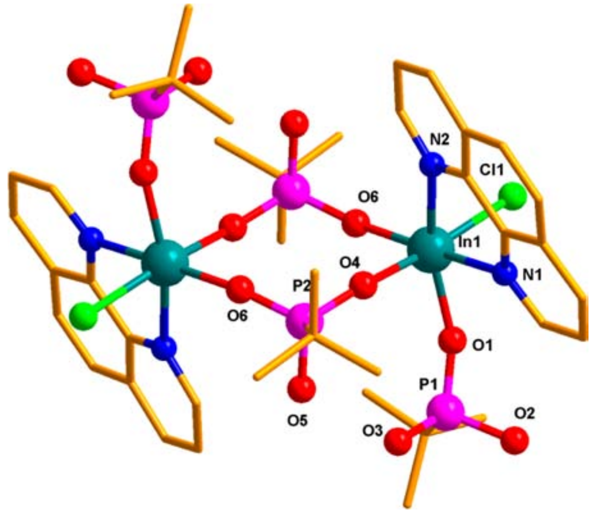
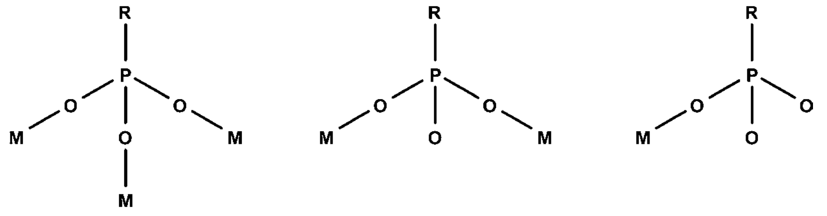


Figure 1. Molecular structure of **1**. All hydrogen atoms have been omitted for clarity. Important bond lengths (Å): In1–O1 2.117(3), In1–O4 2.113(4), In1–O6 2.099(3), In1–N1 2.298(4), In1–N2 2.312(4), In1–Cl1 2.432(1), P2–O4 1.508(4), P2–O6 1.515(4), P2–O5 1.563(4), P1–O1 1.509(4), P1–O2 1.576(4), P1–O3 1.514(4).

The two P–O bond distances found in **1** (involved in the bridging coordination) are nearly equal [average: 1.512(4) Å]. The third P–O(H) bond is relatively longer, 1.563(4) Å. The In–O bonds formed by the bridging phosphinate ligands also possess nearly the same distances [average: 2.106(4) Å]. Each of the indium centers is also bound with a unidentate phosphinate ligand, [*t*-BuP(O)$_2$OH]$^-$. As expected in this instance, three types of P–O bonds were observed, with the shortest distance of 1.509(4) Å being associated with O1 that is bound to the metal ion. The coordination modes exhibited by the [*t*-BuP(O)$_2$OH]$^-$ ligand in **1** are summarized in Chart 2. In addition to the phosphinate ligands, each indium center is also bound by a terminal chloride ligand [In–Cl 2.432(1) Å] and a chelating phenanthroline ligand [In–N 2.298(4) and 2.312(4) Å]. The other important bond parameters for this compound are summarized in the caption of Figure 1. As a result of the cumulative coordination, both of the indium(III) centers in **1** are six-coordinate (2N, 3O, and Cl) in a distorted octahedral configuration (Figure 1; see also the Supporting Information). Compound **1** is involved in a supramolecular assembly formation that is mediated through intermolecular hydrogen-bonding interactions [2.804(1) Å] between the coordinated chloride and the hydrogen atoms of the phenanthroline ligand (Supporting Information). It was of interest to see the type of supramolecular architecture that would be present in the crystal lattice if the phenanthroline ligands were removed. In such a scenario, we find that C–H---Cl interactions between the *t*-Bu groups and the chloride ligands lead to a 3D architecture (Supporting Information).

The crystal structure of compound **2** contains two crystallographically independent molecules. Some important bond parameters for this compound are summarized in the caption of Figure 2. Each complex possesses a trinuclear core (Scheme 2 and Figure 2) with all three indium(III) centers consisting of a six-coordinate (2N and 4O) distorted octahedral configuration (Supporting Information). The triangular In$_3$ core is held together by two bicapping dianionic tripodal phosphonate ligands from the top and bottom of the indium plane. In addition, two bridging monoanionic phosphonates stitch a pair of indium centers, generating a tightly knit trinuclear [In$_3$(RPO$_3$)$_6$] ensemble. As a result of this multiple coordination action of the phosphonate ligands [3.111, 2.101,

Chart 2. Coordination Modes Shown by the [RPO$_3$]$^{2-}$ and [RP(O)$_2$(OH)]$^-$ Ligands in the Present Study[a]



3.111 **2.101** **1.100**

R = *tert*-butyl or cyclopentyl

[a] Mode 3.111 is observed for compound **2**. Modes 2.101 and 1.100 are observed for compounds **1** and **2**.

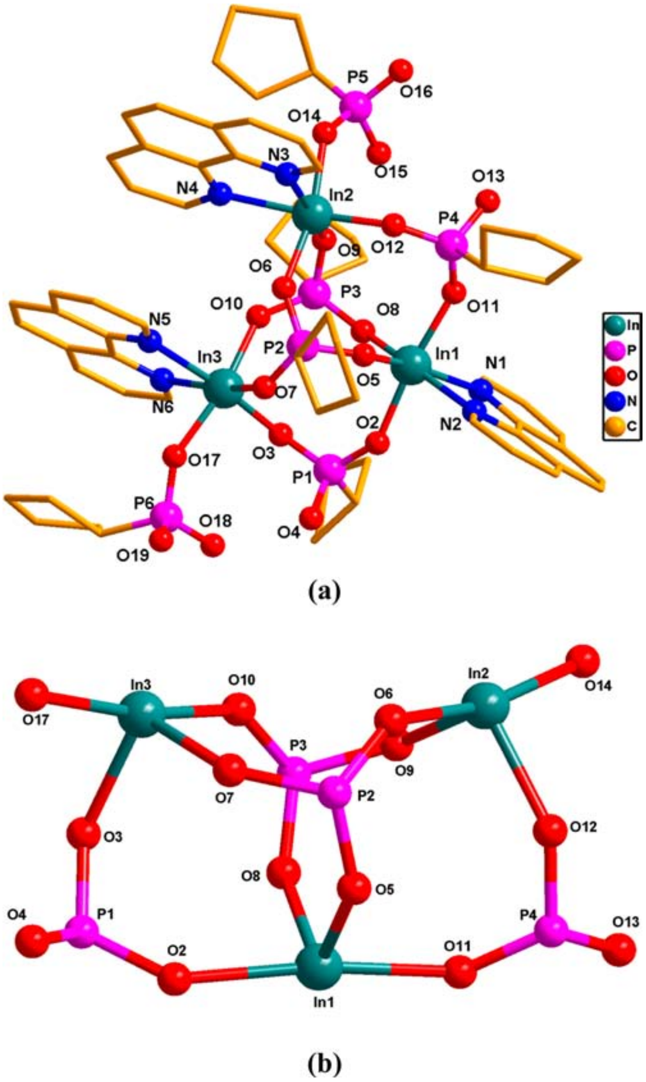


Figure 2. (a) Molecular structure of one of the two independent molecules of **2**. All hydrogen atoms have been omitted for clarity. Important bond lengths (Å): In1−O2 2.134(7), In1−O5 2.089(7), In1−O8 2.076(7), In1−O11 2.105(7), In1−N1 2.264(8), In1−N2 2.274(9), In2−O6 2.102(7), In2−O9 2.121(7), In2−O12 2.087(6), In2−O14 2.132(8), In2−N3 2.273(9), In2−N4 2.279(9), In3−O3 2.093(7), In3−O7 2.096(7), In3−O10 2.113(7), In3−O17 2.111(7), In3−N5 2.274(9), In3−N6 2.269(10), P1−O2 1.508(7), P1−O3 1.508(8), P1−O4 1.570(9), P2−O5 1.510(7), P2−O6 1.524(7), P2−O7 1.533(7), P3−O8 1.504(7), P3−O9 1.524(7), P3−O10 1.528(8), P4−O11 1.490(7), P4−O12 1.518(7), P4−O13 1.498(10). (b) In−O−P core of **2**.

and 1.100 (Harris notation); see Chart 2][27] six In−O−P-containing eight-membered rings are formed in the structure of **2** (Figure 2b). To the best of our knowledge, this structural motif is unique and has been found for the first time among any metal phosphonate structures. Previously known trinuclear metal phosphonate ensembles do not involve the additional bridging coordination interaction of the two terminal phosphonate ligands.[1] The three indium centers in **2** are organized in the corners of a triangle with unequal In−In distances: molecule 1, In1−In2 4.511(1) Å; In1−In3 4.537(1) Å, and In2−In3 5.004(2) Å; molecule 2, In4−In5 4.424(1) Å, In4−In6 5.003(2) Å, and In5−In6 4.558(1) Å (Supporting Information). For each molecule, the monocoordinated phosphonates are connected to the indium centers that are further apart, namely, In2−In3 and In4−In6. Phenanthroline ligands attached to these indium centers are involved in intramolecular $\pi\cdots\pi$ interactions [centroid−centroid distances, 3.819(1) and 3.748(1) Å, respectively]. Intermolecular $\pi\cdots\pi$ interactions are observed between these and the phenantholine ligands attached to the other indium centers, In5 and In1 [centroid−centroid distances, 3.480(1) and 3.709(1)/3.627(1) Å, respectively] (Supporting Information).

Solid-State NMR, Fluorescence, and Thermal Analysis. The solid-state MAS ^{31}P NMR spectrum of complex **1** (Supporting Information) shows two signals at δ 21.9 and 29.3. The integral ratio of 1:1 is consistent with the two crystallographically different atoms found in the crystal structure. For complex **2**, there are a total of 12 crystallographically different phosphorus atoms, 6 in each of the 2 independent molecules. The solid-state MAS ^{31}P NMR spectrum (Supporting Information) contains signal maxima at δ 25.8 and 28.9, in addition to a shoulder at δ 31.5, indicating fortuitous coincidence of the chemical shifts. A low-intensity signal is seen at δ 20.1; this appears to be due to an impurity.

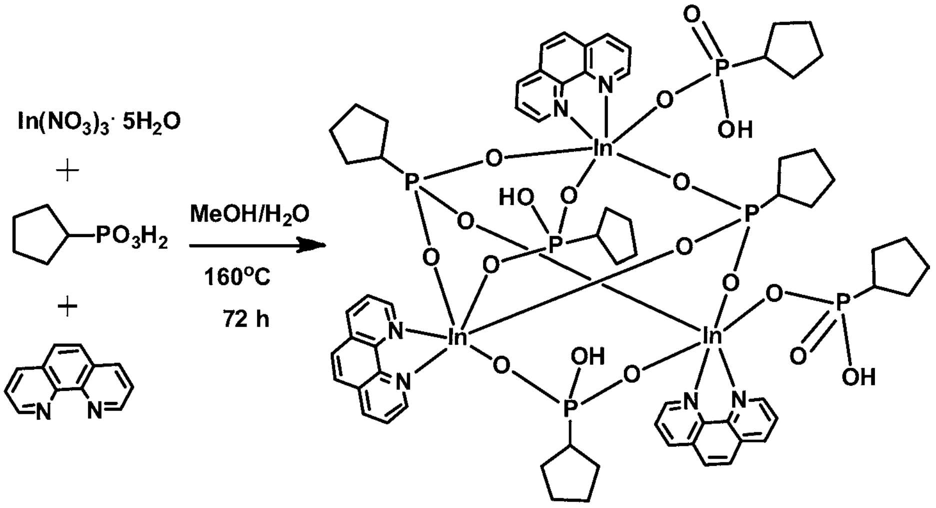
Room temperature solid-state fluorescence spectra of **1** and **2** are characterized by a strong emission band at 385 nm (λ_{ex} = 350 nm) and 395 nm (λ_{ex} = 350 nm), respectively (Supporting Information). The spectrum of **1** also has a shoulder at 406 nm, while that of complex **2** is also characterized by the presence of a hump on the red side of the main band around 415 nm. The free phenanthroline·H_2O shows two fluorescent bands with maxima at 365 and 388 nm.[28,29] The red shift of the phenanthroline emission bands in **1** and **2** is perhaps due to the intermolecular excimer-type interactions between phenanthroline ligands that are maintained by the indium metal centers.[28] The insolubility of **1** and **2** in any solvent precluded such studies in solution.

The TGA study of complex **1** shows mainly a two-step gradual weight loss process (Supporting Information). The first event between 40 and 355 °C corresponds to a small weight loss, ∼11%, which is probably due to the loss of one phosphonate ligand. The second step (390−415 °C) corresponds to a further weight loss of ∼20% (loss of two chloride and 1,10-phenanthroline ligands). The final char yield at 800 °C is 36%. The PXRD of the char yield (Supporting Information) does not correspond to any pure indium phosphate phase. TGA of complex **2** also shows mainly a two-step gradual weight loss (Supporting Information). The first step between 40 and 305 °C corresponds to a weight loss of ∼21% (loss of noncoordinated water molecules, one nitrate anion, and two cyclopentyl phosphonates). The second step (305−315 °C) corresponds to a weight loss of ∼9% (1,10-phenanthroline). At 800 °C, the char yield is 14%. In this instance also, the PXRD of the char yield does not match a pure indium phosphate phase (Supporting Information).

■ CONCLUSION

We report the first examples of molecular indium(III) phosphonates. Two compounds, a dinuclear derivative and a trinuclear aggregate, were prepared by the reaction of indium(III) salts, an organophosphonic acid, and phenanthroline using solvothermal synthetic methods. Complex **1**, the dinuclear derivative, contains two indium(III) centers that are bridged by isobidentate phosphonate ligands, $[t\text{-BuP(O)}_2\text{OH}]^-$, resulting in an eight-membered $(In_2P_2O_4)$ puckered ring. Complex **2**, the trinuclear ensemble, contains

Scheme 2. Synthesis of 2



a triangular In$_3$ platform held together by bicapping tripodal phosphonate ligands from the top and bottom of the indium plane and two bridging monoanionic phosphonate ligands connecting two pairs of indium(III) centers. **1** and **2** are stabilized in the solid state through weak interactions (hydrogen-bonding/$\pi-\pi$ interactions), which results in a red shifting of their emission in comparison to free phenanthroline. The solution studies of these compounds could not be carried out because of their insolubility. We are trying to design and use highly lipophilic phosphonic acids that would allow us to prepare soluble molecular indium(III) phosphonates.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, bond lengths and angles of **1** and **2**, coordination geometry, structures, hydrogen-bonding interactions, spectra, TGA curves, and PXRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: vc@iitk.ac.in or vc@tifrh.res.in.

Notes

The authors declare no competing financial interest.

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