

Zero- or One-Dimensional Organic-Inorganic Hybrid Polyoxoniobates Constructed from Decaniobate Units and Transition-**Metal Complexes**

Jingyang Niu,[†] Guan Wang,[†] Junwei Zhao,[†] Yunxia Sui,[‡] Pengtao Ma,[†] and Jingping Wang^{*,†}

[†]Institute of Molecular and Crystal Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, P. R. China

[‡]Center of Modern Analysis, Nanjing University, Nanjing, Jiangsu 210093, P. R. China

Supporting Information

 $\begin{array}{l} \textbf{ABSTRACT:} & \text{A series of novel organic-inorganic hybrids containing } [Nb_{10}O_{28}]^{6-} & \text{building blocks } [Ni(2,2'\text{-bipy})_2]_3 \\ [Nb_{10}O_{28}] \cdot 2H_2O & (1), \\ [Ni(2,2'\text{-bipy})_3] \{ [Ni(2,2'\text{-bipy})_2]_2 [Nb_{10}O_{28}] \} \cdot 8.5H_2O & (2), \\ [M(\text{phen})_3] \{ [M(\text{phen})_2]_2 [Nb_{10}O_{28}] \} \cdot 8H_2O \\ (M = Ni^{II} \text{ for 3}; \\ M = Zn^{II} \text{ for 4}; \\ M = Co^{II} \text{ for 5} & (2,2'\text{-bipy})_2 - 2,2'\text{-bipydine, phen} = 1,10\text{-phenanthroline} \\ \end{array} \right) \\ \begin{array}{l} \text{Abstract} \\ \text{Abstra$ synthesized using the hydrothermal method by introducing different transition-metal complexes and fully characterized by elemental analyses, X-ray powder diffraction (XRPD), IR spectroscopy, UV spectroscopy, single-crystal X-ray diffraction analyses, and thermogravimetric analyses. 1 is a one-dimensional (1D) infinite chain polyoxoniobate built by $[Nb_{10}O_{28}]^{6-}$ units and $[Ni(2,2'-bipy)_2]_3^{6+}$ cations. Furthermore, adjacent chains in 1 are further interacted by $\pi - \pi$ stacking interactions resulting in a three-dimensional (3D) supramolecular network. 2-5 are constructed from $[Nb_{10}O_{28}]^{6-}$ units and different transition-metal complexes, in which neighboring units are combined together via the $\pi - \pi$ interactions between pyridine rings of ligands forming a 1D linear supramolecular chain. Moreover, the photoluminescence properties of 1 and 3-5 have been investigated. Electron paramagnetic resonance (EPR) spectra reveal that high-spin Co^{II} ions in 5 inhibit the octahedral environments.

INTRODUCTION

Polyoxometalates (POMs) as fascinating species of inorganic compounds have a wide range of potential applications in catalysis, materials science, chemical biology, medicine, and nanotechnology.¹ As a unique branch of POMs, polyoxoniobates (PONs) also display multiple applications in virology, nuclearwaste treatment, and the base-catalyzed decomposition of biocontaminants.² In comparison with other POMs species which are steady over a wide pH range, PONs always require alkaline conditions (10.5-12.5) to exist stably.³ Because of the inertness of niobium-oxo clusters, PON chemistry remains less explored to date.

Although the hexaniobate cluster $[Nb_6O_{19}]^{8-}$ was obtained as early as 1953,⁴ the PON chemistry did not attract much attention until the late 1960s. Flynn et al. reported the dimeric structure of $[M(Nb_6O_{19})_2]^{12-}$ ($M = Mn^{IV}$, Ni^{IV}) in 1969.⁵ In 1977, the decaniobate ion $[Nb_{10}O_{28}]^{6-}$ was determined.⁶ In 1994, Yamase and co-workers synthesized a high-nuclearity oxoniobate complex { $[Eu_3O(OH)_3(OH_2)_3]_2Al_2(Nb_6O_{19})_5$ }²⁶⁻ based on two trimeric oxohydroxoaquo europium clusters coordinated by two Al^{3+} cations and five $[Nb_6O_{19}]^{8-}$ anions.⁷ In 2001, Pope and coworkers isolated a class of tricarbonyl metal derivatives of hexaniobate anions $[Nb_6O_{19}{M(CO)_3}_n]^{(8-n)-}$ (M = Re^I, Mn^{I} ; n = 1, 2).⁸ In the following years, Nyman's group communicated a large number of heteropolyoxoniobates: in 2002, they synthesized the Keggin-type heteropolyniobate cluster $\{[Ti_2O_2][SiNb_{12}O_{40}]\}^{12-}$ and the lacunary derivative $[H_2Si_4Nb_{16}O_{56}]^{14-}$ under hydrothermal conditions.⁹ Then a series of Keggin-based dodecaniobates $[TNb_{12}O_{40}]^{16-,10}$ $[Ti_2O_2][TNb_{12}O_{40}]^{12-,2f}$ and $[Nb_2O_2][TNb_{12}O_{40}]^{10-}$ were

published (T = Si^{IV}, Ge^{IV}).^{2f} In 2006, a trivacant α -Keggin ion [(PO₂)₃PNb₉O₃₄]¹⁵⁻ decorated by PO²⁺ was presented.²¹ Subsequently, Yagasaki et al. prepared a icosaniobate [Nb₂₀O₅₄]⁸⁻, which can be considered as a fusion of two decaniobate anions by which can be considered as a fusion of two decaniobate anions by sharing two terminal O atoms.¹² In recent years, Nyman's group also reported several isopolyoxoniobates $[Nb_{24}O_{72}H_9]^{15-13}$, $[(Nb_6O_{19}H_2)_2Cu(en)_2]^{10-14}$, $[(Nb_6O_{19}H_2)Cu(en)_2]^{4-}$, $\{[Nb_6O_{19}][Cu(NH_3)_2]_2^{8-14}$, $\{[Nb_6O_{19}][Cu(NH_3)_2(H_2O)]_2$, $[Cu(H_2O)_4]_2\} \cdot 3H_2O$,¹⁴ and $\{[Nb_6O_{19}][Cu(NH_3)_2(H_2O)]_2$, $[Cu(H_2O)_4]_2\}^{14}$ has 2009. Use at all illustrations in the second secon $[Cu(H_2O)_4]_2$.¹⁴ In 2008, Hu et al. illustrated two decaniobates constructed from $[Nb_{10}O_{28}]^{6-}$ and M(2,2'-bipy) (M = Co^{II}, Zn^{II}).¹⁵ In the same year, Casey and co-workers addressed a novel superoctahedral polyoxo- titanoniobate [Ti₁₂Nb₆O₄₄]¹⁰⁻ containing a cubic $[Ti_{12}O_{14}]^{20+}$ core, of which each face was capped by a $[NbO_5]^{5-}$ unit.¹⁶ Recently, Cronin's group separated two gigantic isopolyoxoniobates $[HNb_{27}O_{76}]^{16-}$ and $[H_{10}Nb_{31} O_{93}(CO_3)]^{23-}$ built from pentagonal $\{Nb(Nb)_5\}$ units.17

Since 2005, our group has been making great efforts to explore the PON system. In 2007, we addressed a family of giant PON clusters $[({KNb_{24}O_{72}H_{10,25}}{Cu (en)_2})_2{Cu_3(en)_3(H_2O)_3} {Na_{1.5}Cu_{1.5}(H_2O)_8}]^{11-}, [H_{23}Na O_8Cu_{24}(Nb_7O_{22})_8]^{16-} and [H_9Cu_{25.5}O_8(Nb_7O_{22})_8]^{28-}$ by the conventional aqueous solutional solution of the conventional solution of the convention of tion method, which are all based on $[Nb_7O_{22}]^{9-}$ units derived from Nb_6O_{19} precursors.¹⁸ Afterward, a novel hexaniobate {Nb₆O₁₉ $[Cu(2,2'-bipy)]_2[Cu(2,2'-bipy)_2]_2$ · 19H₂O was

```
Received:
            November 9, 2010
Revised:
            January 13, 2011
Published: February 08, 2011
```

made by the rational self-assembly strategy.¹⁹ Although the diffusion technique is widely used and provides an effective method for crystal growth in supramolecular chemistry and coordination chemistry,²⁰ it is uncommon to be employed in the synthesis of POMs, especially for PONs. Recently, two novel copper-undecaniobates decorated by copper-organic cations $[{Cu(H_2O)L}_2 {CuNb_{11}O_{35}H_4}]^{5-}$ (L = phen, 2,2'-bipy) were communicated by us by means of the diffusion method.²¹ Meanwhile, by introducing mixed ligands to the hexaniobate system, three novel 2D organic-inorganic hybrids $[Cu(L_1)_2]_2\{[Cu(L_2)][Cu(L_2)(H_2O)] Nb_6O_{19}\} \cdot nH_2O (L_1 =$ en or 1,2-dap, L_2 = phen or 2,2'-bipy) were synthesized by the same method.²² In this paper, we explored the reaction behavior of the $[Nb_6O_{19}]^{8-}$ precursor with transition-metal cations in the presence of 2,2'-bipy or phen under hydrothermal conditions. Finally, five novel PONs $[Ni(2,2'-bipy)_2]_3[Nb_{10}O_{28}]\cdot 2H_2O$ $[Ni(2,2'-bipy)_3]{[Ni(2,2'-bipy)_2]_2[Nb_{10}O_{28}]} \cdot 8.5H_2O_{28}$ (1), (2), $[M(phen)_3]{[M(phen)_2]_2 [Nb_{10}O_{28}]} \cdot 8H_2O$ (M = Ni^{II} for 3; $M = Zn^{II}$ for 4; $M = Co^{II}$ for 5) were obtained and characterized by elemental analyses, X-ray powder diffraction (XRPD), IR spectroscopy, UV spectroscopy, single-crystal X-ray diffraction, thermogravimetric analyses, photoluminescence properties, and EPR spectra. The common feature is that these PONs are all constructed from $[Nb_{10}O_{28}]^{6-}$ units and transition-metal complexes. 1 is a 1D infinite chain PON built by $[\mathrm{Nb_{10}O_{28}}]^{6-}$ units and $[\mathrm{Ni}(2,2'\text{-bipy})_2]_3^{6+}$ cations. Furthermore, adjacent chains in 1 are further interacted by $\pi - \pi$ stacking interactions resulting in a 3D supramolecular network. 2-5 are constructed from $[Nb_{10}O_{28}]^{6^{-1}}$ units and different transitionmetal complexes. Neighboring units in 2-5 are combined together via the $\pi - \pi$ interactions between pyridine rings of ligands forming a 1D linear supramolecular chain. To our knowledge, 1-3 represent the first examples of organicinorganic hybrid nickel-containing decaniobates. More interestingly, the phenomenon that the $[Nb_6O_{19}]^{8-}$ precursor transformed to the $[Nb_{10}O_{28}]^{6-}$ cluster was observed in the preparations of 1–5. Although the $[Nb_{10}O_{28}]^{6-}$ cluster has been known for several decades, decaniobate-based organicinorganic hybrids are rarely reported until now.¹⁵ In the present paper, a detailed study on the influence of organic ligands and transition-metals on the formation of decaniobate compounds is conducted.

EXPERIMENTAL SECTION

General Methods and Materials. All reagents were used as purchased without further purification. K7HNb6O19.13H2O was synthesized according to ref 23 and identified by IR spectrum. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400-II CHNS/O analyzer. IR spectra were recorded on a Nicolet 360 FT-IR spectrometer using KBr pellets in the range of 4000-400 cm⁻¹. UV spectra were obtained on a HITACHI U-4100 UV-vis-NIR spectrometer (distilled water as solvent) in the range of 400-190 nm. Emission/excitation spectra were recorded on a HITACHI F-7000 fluorescence spectrophotometer. Thermogravimetric (TG) analyses were carried out on a Mettler-Toledo TGA/SDTA 851^e thermal analyzer in a flowing air atmosphere in the temperature region of 25-800 °C with a heating rate of 10 °C · min⁻¹. X-ray powder diffraction (XRPD) measurements were taken by a Philips X'Pert-MPD instrument with Cu K α radiation (λ = 1.54056 Å) at 293 K. Electron paramagnetic resonance (EPR) spectra of 1, 3, and 5 were obtained on a Bruker ER-2000-DSRC10 spectrometer at the X-band at 300 and 110 K.

Syntheses of 1 and 2. A mixture of $K_7HNb_6O_{19} \cdot 13 H_2O$ (0.045 g, 0.033 mmol), $Ni(NO_3)_2 \cdot 6H_2O$ (0.029 g, 0.100 mmol), 2,2'-bipy (0.047 g, 0.300 mmol), $Na_2S_2O_3 \cdot 5H_2O$ (0.050 g, 0.200 mmol), and H_2O (8 mL, 444 mmol) was stirred for 10 h, and then the pH value was adjusted to 11.4 using NaOH (0.250 mol·L⁻¹) solution. The resulting suspension was transferred to a Teflon-lined autoclave (20 mL) and kept at 120 °C for 3 days. After slow cooling to room temperature, light blue small cubic crystals of 1 and purple large cubic crystals of 2 were obtained by filtering and were separated manually. Yield: ca. 16% for 1, 25% for 2 (based on $K_7HNb_6O_{19} \cdot 13H_2O$). Anal. Calcd. (found %) for $C_{60}H_{52}$ $N_{12}Nb_{10}Ni_3O_{30}$ (1): C 28.53 (28.41), H 2.07 (2.16), N 6.65 (6.70); Anal. Calcd. (found %) for $C_{70}H_{73}N_{14}Nb_{10}$ $Ni_3O_{36.5}$ (2): C 30.03 (29.92), H 2.63 (2.70), N 7.00 (7.06).

Synthesis of 3. The synthetic procedure was identical to 1 and 2, but phen (0.039 g, 0.200 mmol) was used as an organic ligand. Green cubic crystals were collected after 3 days. Yield: ca. 27% (based on $K_7HNb_6O_{19} \cdot 13H_2O$). Anal. Calcd. (found %) for $C_{84}H_{72}N_{14}Nb_{10}Ni_3O_{36}$ (3): C 34.10 (34.00), H 2.45 (2.52), N 6.63 (6.68).

Synthesis of 4. 4 was prepared according to the method of 1 and 2, but $Zn(NO_3)_2 \cdot 6H_2O$ (0.029 g, 0.100 mmol) was used instead of $Ni(NO_3)_2 \cdot 6H_2O$. The amount of phen and $Na_2S_2O_3 \cdot 5H_2O$ was changed to (0.019 g, 0.100 mmol) and (0.025 g, 0.100 mmol), respectively. After 3 days, white cubic crystals were collected. Yield: ca. 22% (based on $K_7HNb_6O_{19} \cdot 13H_2O$). Anal. Calcd. (found %) for $C_{84}H_{72}N_{14}Nb_{10}Zn_3O_{36}$ (4): C 33.87 (33.75), H 2.44 (2.50), N 6.58 (6.68).

Synthesis of 5. 5 was prepared similar to 1 and 2, but Co- $(NO_3)_2 \cdot 6H_2O$ (0.029 g, 0.100 mmol) was used and the amount of $Na_2S_2O_3 \cdot 5H_2O$ was changed to (0.025 g, 0.100 mmol). After 3 days, orange cubic crystals were collected. Yield: ca. 25% (based on $K_7HNb_6O_{19} \cdot 13H_2O$). Anal. Calcd. (found %) for $C_{84}H_{72}N_{14}Nb_{10}Co_3O_{36}$ (5): C 34.09 (33.96), H 2.45 (2.54), N 6.63 (6.69).

X-ray Crystallography. A crystal with dimensions $0.21 \times 0.18 \times$ 0.17 mm^3 for 1, $0.34 \times 0.33 \times 0.27 \text{ mm}^3$ for 2, $0.21 \times 0.14 \times 0.09 \text{ mm}^3$ for 3, $0.35 \times 0.23 \times 0.16$ mm³ for 4, and $0.34 \times 0.29 \times 0.25$ mm³ for 5 was stuck on a glass fiber, and intensity data were collected on a Bruker Apex-II CCD detector using graphite monochromatized Mo Ka radiation ($\lambda = 0.71073$ Å) at room temperature. Routine Lorentz and polarization corrections were applied. The absorption correction was based on multiple and symmetry-equivalent reflections in the data set by using the SADABS program. The structures were solved by direct methods and refined using full-matrix least squares on F^2 . All calculations were performed using the SHELXTL-97 program package.²⁴ No hydrogen atoms associated with the molecules were located from the difference Fourier map. Positions of the hydrogen atoms attached to the carbon atoms were geometrically placed. All hydrogen atoms were refined isotropically as a riding mode using the default SHELXTL parameters. All non-hydrogen atoms were refined anisotropically except for some carbon atoms and water molecules. A summary of crystal data and structure refinements for 1-5 was listed in Table 1. CCDC reference nos. are 792550, 792551, 792552, 792553, and 792554 for 1-5, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data request/cif.

RESULTS AND DISCUSSION

Synthesis. Owing to the chemical inertness and insolubility of amorphous Nb₂O₅, it is very difficult to directly prepare PONs using Nb₂O₅ as the starting material. To date, the majority of reported PONs was synthesized by $[Nb_6O_{19}]^{8-}$ precursors. Scheme 1 summarizes the typical PONs derived from

Table 1.	Crystallographic	Data and Structural	Refinements	for 1	l-5
----------	------------------	---------------------	-------------	-------	-----

	1	2	3	4	5		
formula	C ₆₀ H ₅₂ N ₁₂ Nb ₁₀ Ni ₃ O ₃₀	C ₇₀ H ₇₃ N ₁₄ Nb ₁₀ Ni ₃ O _{36,50}	C ₈₄ H ₇₂ N ₁₄ Nb ₁₀ Ni ₃ O ₃₆	C ₈₄ H ₇₂ N ₁₄ Nb ₁₀ Zn ₃ O ₃₆	C ₈₄ H ₇₂ N ₁₄ Nb ₁₀ Co ₃ O ₃₆		
$M_{\rm r} ({\rm g}{ m mol}^{-1})$	2526.26	2799.55	2958.69	2978.78	2959.41		
T (K)	296(2)	296(2)	296(2)	296(2)	296(2)		
space group	C_2/c	$P\overline{1}$	C ₂ /c	C ₂ /c	C_2/c		
crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic		
a (Å)	24.250(7)	14.139(3)	27.578(10)	27.946(4)	27.771(3)		
b (Å)	18.765(6)	14.160(3)	17.319(6)	17.356(2)	17.263(2)		
c (Å)	17.720(5)	24.201(5)	24.646(9)	24.704(3)	24.677(5)		
α (deg)	90	80.884(3)	90	90	90		
β (deg)	107.673(4)	89.686(3)	121.555(6)	121.284(2)	121.158(2)		
γ (deg)	90	89.727(3)	90	90	90		
$V(Å^3)$	7683(4)	4784.2(15)	10031(6)	10240(2)	10124(2)		
Z	4	2	4	4	4		
$D_{\rm c} ({\rm g \ cm}^{-3})$	2.184	1.811	1.959	1.932	1.942		
$\mu \ (\mathrm{mm}^{-1})$	2.236	2.488	1.733	1.849	1.651		
limiting indices	$-22 \le h \le 28$	$-16 \le h \le 15$	$-34 \le h \le 34$	$-20 \le h \le 34$	$-33 \le h \le 34$		
	$-22 \le k \le 16$	$-16 \le k \le 13$	$-21 \le k \le 14$	$-21 \le k \le 21$	$-13 \le k \le 21$		
	$-21 \le l \le 20$	$-28 \le l \le 27$	$-30 \le l \le 25$	$-27 \le l \le 30$	$-30 \le l \le 28$		
GOF on F^2	1.039	1.065	1.002	1.008	1.004		
$R_1^{a}, w R_2^{b} [I > 2\sigma(I)]$	0.0220, 0.0595	0.0384, 0.1031	0.0577, 0.1305	0.0526, 0.1158	0.0360, 0.1042		
R_1^{a} , wR_2^{b} [all data]	0.0263, 0.0614	0.0553, 0.1102	0.1251, 0.1653	0.1235, 0.1493	0.0484, 0.1170		
${}^{t}R_{1} = \Sigma F_{0} - F_{c} / \Sigma F_{c} ; {}^{b}wR_{2} = \Sigma [w(-)^{2}] / \Sigma [w()^{2}]^{1/2}$ with $1/w = \sigma^{2} + aP^{2} + bP$ and $P = +2/3$.							





 $[Nb_6O_{19}]^{8-}$ as precursors in the past decade.^{2h,2-} f,8,11–14,17,18,21,22,25,26 In PON chemistry, first-row transition-metal ions introduced into PONs are well-known, and a

large number of such complexes have been reported to date. However, most of the published works were based on Cu^{II} ions. 14,18,21,22 As a result, we want to explore the hydrothermal



Scheme 2. Typical Isopolyoxoniobates Derived from the Lindqvist-type Anion $\left[\mathrm{Nb}_6\mathrm{O}_{19}
ight]^{8-1}$

reaction of $[Nb_6O_{19}]^{8-}$ precursors with other transition-metals in the presence of organic ligands to synthesize novel PONs. When Fe^{III} ions and 2,2'-bipy were initially employed, only amorphous powders were obtained. When Co^{II} ions replaced Fe^{III} ions, a reported PON $[Co(2,2'-bipy)_2]_3$ $[Nb_{10}O_{28}] \cdot$ $1.5H_2O$ was isolated.¹⁵ To our knowledge, only two Ni^{II}-containing PONs were reported.^{27a} Thus, nickel ions were introduced, and one-pot hydrothermal reaction led to the formation of 1 and 2 with different appearances and colors. Such a phenomenon that one-pot hydrothermal reaction resulted in the formation of two species was previously observed.^{27b} Under a similar procedure, another reported PON $[Zn(2,2'-bipy)_2]_3[Nb_{10}O_{28}] \cdot 3H_2O$ was afforded.¹⁵ Hitherto, we have failed to isolate the Cu^{II}-containing analogue.

To further investigate the structural diversity that can be tuned by the nature of different organic ligands, phen was introduced to replace 2,2'-bipy. Using the reaction system similar to 1 and 2 resulted in 3. When Co^{II} ions were replaced by Ni^{II} ions, 5 was obtained. When Zn^{II} ions were used, 4 was discovered. When Fe^{III} ions and Cu^{II} ions were employed, no crystal was observed in the autoclave. Nevertheless, other aromatic N-ligands such as 4,4'-bipy, diimidazole, and 2-(1H-pyrazol-3-yl)-pyridine were also investigated, and no analogous species were separated. Therefore, organic ligands play a key role in the formation of the products.

Considering the influence of the pH value on final reaction products, parallel experiments were performed. 1-5 could be successfully prepared in the pH value of approximately 11.3-11.4. When the pH value was lower than 11.3, amorphous powders were formed. On the contrary, when the pH value was higher than 11.4, clear solutions were afforded. Notably, although Na₂S₂O₃ was used as a staring material in the system, no sodium or sulfur atoms were observed in these compounds. When Na₂S₂O₃ was removed from the reaction, amorphous powders were afforded. The specific role of Na₂S₂O₃ was not well understood, and $Na_2S_2O_3$ may play a synergistic action with other components in the reaction. Similar phenomena have been previously encountered.^{27c,27d}

In the upcoming investigation, we will continue to probe and explore the formation mechanism and the pertinent synthetic chemistry. Moreover, the research on the assembly of hexaniobate precursors with other transition-metal or rare-earth cations is in progress.

Structural Descriptions. The experimental XRPD patterns of the bulk products of 1-5 are in good agreement with the simulated XRPD patterns from single crystal X-ray diffraction, indicating the phase purity of the sample (Figure S1, Supporting Information). The intensity difference between experiment and simulation XRPD patterns is due to the variation in the preferred orientation of the powder sample during collection of the experimental XRPD. X-ray structural analyses reveal that 1-5 are all constructed from the $[Nb_{10}O_{28}]^{6-}$ unit and metalorganic complexes. 1 and 3-5 belong to the monoclinic space group C_2/c , while 2 crystallizes in the triclinic space group $P\overline{1}$ (Table 1). The $[Nb_{10}O_{28}]^{6-}$ polyoxoanion in 1-5 is a highly condensed system of NbO₆ octahedra, which are arranged through 10 Nb and 28 O atoms. Actually, similar decavanadate was also encountered in a previous study. In 2001, Jacobson et al. reported a copper 2-pyrazinecarboxylate (2-pzc) coordination polymer $Cu_3(2\text{-}pzc)_4(H_2O)_2(V_{10}O_{28}H_4)\cdot 6.5H_2O$ incorporating $[V_{10}O_{28}H_4]^{2^-}$ polyanions.²⁸ Notably, in the formation of 1-5, the phenomenon that the $[Nb_6O_{19}]^{8-}$ polyoxoanion is transformed to the $[Nb_{10}O_{28}]^{6-}$ polyoxoanion has been observed (Scheme 2a,c). On the other hand, the $[Nb_{10}O_{28}]^{6-1}$ polyoxoanion can be viewed as a fusion of two monolacunary Lindqvist $[Nb_5O_{18}]^{11-}$ units (Scheme 2b). Accordingly, the $[Nb_6O_{19}]^{8-}$ polyoxoanion is able to isomerize to the isoniobate anion $[Nb_{20}O_{54}]^{8-}$, which is composed of four monolacunary Lindqvist $[Nb_5O_{18}]^{11-}$ units (Scheme 2d).¹² Very recently, we proved that the $[Nb_6O_{19}]^{8-}$ polyoxoanion can transform to the

Table 2. Selected Bond Lengths [Å] for 1-5 (M = Ni^{II}, Zn^{II}, Co^{II})

A-X	1	2	3	4	5
Nb-O _t	1.729(2)-1.772(2)	1.726(4)-1.764(3)	1.714(7)-1.770(6)	1.723(6)-1.773(5)	1.730(4)-1.775(3)
Nb- μ_2 -O _b	1.823(2)-2.101(2)	1.817(3)-2.094(4)	1.829(6)-2.089(6)	1.826(6)-2.103(6)	1.824(3)-2.093(3)
Nb $-\mu_3 - O_b$	1.991(2)-2.139(2)	1.976(3) - 2.134(3)	1.988(5)-2.122(6)	1.989(5)-2.133(5)	1.982(3)-2.121(3)
Nb-O _c	2.230(2) - 2.572(2)	2.223(3)-2.561(3)	2.241(5)-2.535(5)	2.242(5)-2.561(5)	2.236(3)-2.539(3)
M-N	2.051(3)-2.115(3)	2.054(5) - 2.112(4)	2.078(8)-2.105(8)	2.137(7)-2.207(8)	2.116(4)-2.164(4)
М-О	2.054(2) - 2.087(2)	2.043(4) - 2.099(4)	2.051(6)-2.101(6)	2.083(5) - 2.151(6)	2.064(3)-2.106(3)

 $[CuNb_{11}O_{35}H_4]^{9-}$ polyoxoanion in the participation of the Cu^{II} cation (Scheme 2e).²¹ The $[CuNb_{11}O_{35}H_4]^{9-}$ polyoxoanion can be looked on as a monolacunary Lindqvist $[Nb_5O_{18}]^{11-}$ unit combining with a plenary Lindqvist $[Nb_6O_{19}]^{8-}$ unit accompanying incorporation of one Cu^{II} ion to the pocket.²¹ In addition, the phenomena that the $[Nb_6O_{19}]^{8-}$ polyoxoanions convert to other polyoxoniobate anions have been also discovered.^{13,17,18} For example, in 2006 and 2007, both Nyman's group and our group observed that the $[Nb_6O_{19}]^{8-}$ polyoxoanion can evolve to the monocapped Lindqvist [Nb₇O₂₂]⁹⁻ fragment (Scheme 2f).^{13,18} More interestingly, the $[Nb_7O_{22}]^{9-}$ fragments can further polymerize to the novel larger aggregates $[Nb_{24}O_{72}H_9]^{15-}$ containing three $[Nb_7O_{22}]^{9-}$ fragments linked by three NbO_6 octahedra¹³ (Scheme 2g) and $[H_9Cu_{25.5}O_8(Nb_7O_{22})_8]^{28}$ constructed by eight $[Nb_7O_{22}]^{9}$ fragments and a $\{Cu_{25.5}O_8\}$ subunit ¹⁸ (Scheme 2h). It should be noted that Cronin et al. illustrated that the $[Nb_6O_{19}]^{8-}$ polyoxoanions can transform to the [HNb₂₇O₇₆]¹ and $[H_{10}Nb_{31}O_{93}(CO_3)]^{23-}$ clusters by means of the combination of the hydrothermal technique and the evaporation method.¹⁷ The above-mentioned results show that the $[Nb_6O_{19}]^{8-}$ polyoxoanion can work as the active reaction precursor if the optimum reaction conditions are discovered.

In the $[Nb_{10}O_{28}]^{6-}$ polyoxoanions of 1–5, the Nb–O distances lie in the 1.714(7)–1.775(3) Å for the terminal oxygen atoms $(Nb-O_t)$, 1.817(3)–2.103(6) Å for double bridging oxygen atoms $(Nb-\mu_2-O_b)$, 1.976(3)–2.139(2) Å for triple bridging oxygen atoms $(Nb-\mu_3-O_b)$, and 2.223(3)–2.572(2) Å for the central bridging oxygen $(Nb-O_c)$. The Nb–O–Nb bond angles fall in the range 83.32(10)–171.3(3)°. The geometric parameters are in good agreement with those in reported $[Nb_{10}O_{28}]^{6-}$ structures.⁶ The selected bond lengths of 1–5 are listed in Table 2.

X-ray diffraction analysis reveals that 1 exhibits a 1D infinite chain. The structural unit of 1 consists of a $[Nb_{10}O_{28}]^{6-1}$ polyoxoanion, three Ni^{II} cations, six 2,2'-bipy molecules, and two lattice water molecules (Figure 1a), in which there are two crystallographically unique Ni^{II} centers (Ni1 and Ni2). The Ni1 cation is situated on the usual site with an occupancy factor of 1, while the Ni2 cation occupies the special site with an occupancy factor of 0.5. Two decorative $[Ni1(2,2'-bipy)_2]^{2+}$ cations link to the $[Nb_{10}O_{28}]^{6-}$ polyoxoanion through four O_t atoms. The Ni1 and Ni2 cations display the octahedral geometry defined by four N atoms from two 2,2'-bipy ligands [Ni-N: 2.051(3)-2.115(3) Å, N–Ni–N: 78.06(10) $-171.19(11)^{\circ}$] and two terminal O atoms from the polyoxoanion [Ni $-O_t$: 2.054(2)-2.087(2) Å, O_t -Ni- O_t : 88.87(13)-90.78(9)°]. Interestingly, adjacent $[Nb_{10}O_{28}]^{6-}$ polyoxoanions are combined together via $[Ni2(2,2'-bipy)_2]^{2+}$ bridges forming the 1D chain (Figure 1b), which is very rare in PON chemistry. Similarly the 1D connection mode is widely employed in the polyoxotungstate and polyoxomolybdate chemistry.²⁹ For example, in 2004, we reported two ARTICLE

1D Dawson-type polyoxotungstates, in which adjacent $[P_2W_{18}O_{62}]^{6-}$ polyoxoanions were connected via RE complexes.^{29a} Recently, two 1D zigzag chains constructed from α -Keggin anions $[PMo_{12}O_{40}]^{3-}$ and silver complexes were prepared.^{29b} Furthermore, there are strong $\pi-\pi$ stacking interactions between the nearest parallel aromatic rings of 2,2'-bipy ligands with a vertical distance of ca. 3.79 Å; therefore, 3D supramolecular architecture is constructed by strong $\pi-\pi$ stacking interactions contribute to the stability of **1**.

The molecule of **2** consists of two crystallographically independent one-half $[Nb_{10}O_{28}]^{6-}$ polyoxoanions, one discrete $[Ni(2,2'-bipy)_3]^{2+}$ cation, and two pendent $[Ni(2,2'-bipy)_2]^{2+}$ cations (Figure 2a). Interestingly, the phenomenon that one molecule contains two crystallographically unique one-half polyoxoanions is rarely reported in PON chemistry although it was observed previously in an Anderson-type compound.³⁰ The $[Ni1(2,2'-bipy)]^{2+}$ and $[Ni2(2,2'-bipy)]^{2+}$ cations are the octahedral geometry achieved by four N atoms from two 2,2'-bipy ligands [Ni-N: 2.054(5)-2.092(5) Å] and two terminal O atoms from two $[Nb_{10}O_{28}]^{6-}$ polyoxoanions $[Ni-O_t: 2.043(4)-2.099(4) \text{ Å}]$. The $[Ni3(2,2'-bipy)_3]^{2+}$ cation is also in an octahedral coordination environment defined by six N atoms from three 2,2'-bipy ligands [Ni-N: 2.054(5)-2.112(4) Å].

3-5 are isomorphic and their common feature is that they contain a $[\rm Nb_{10}O_{28}]^{6-}$ polyoxoanion decorated by two $[\rm M(phen)_2]^{2+}$ (M = Ni^{II}, Zn^{II}, Co^{II}) cations. Thus, only the structure of 3 is discussed here. As shown in Figure 3a, 3 is constructed from a $[\rm Nb_{10}O_{28}]^{6-}$ polyoxoanion, a $[\rm Ni(2,2'-bipy)_3]^{2+}$ cationic subunit, two decorative $[\rm Ni(2,2'-bipy)_2]^{2+}$ cations, and eight lattice water molecules. There are two crystallographically independent Ni^{II} centers. The Ni1 center is coordinated to two O_t atoms (O4, O5, O4A, O5A) from the $[\rm Nb_{10}O_{28}]^{6-}$ polyoxoanion and four nitrogen atoms from two phen ligands $[\rm Ni-O_t=2.051(6)-2.101(6)$ Å, Ni-N = 2.081(7)-2.105(8) Å]. In the cationic subunit, the Ni2 center is also in octahedral coordination environment coordinated by six nitrogen atoms from three phen molecules $[\rm Ni-N=2.078(8)-2.104(8)$ Å].

From the view of supramolecular chemistry, the supramolecular 1D chains can be constructed via the $\pi - \pi$ interactions with the distances of closest adjacent aromatic rings of 3.974, 3.999, 3.992, and 3.973 Å for **2**-**5**, respectively (Figures 2b and 3b). Such supramolecular interactions may contribute to the structural stabilization and chemical stability of these compounds.

FT-IR and UV Spectra. IR spectra of 1-5 (Figure S2, Supporting Information) were recorded between 400 and 4000 cm⁻¹ with KBr pellet, which is very useful for the identification of characteristic vibration bands of PONs and organic components in products. IR spectra of 1-5 exhibit similar characteristic vibration bands of the decaniobate polyoxoanion.



Figure 1. (a) Ball-and-stick representation of the structural unit of 1. All H atoms are omitted for clarity. (b) A polyhedral and ball-stick representation of the 1D chainlike architectures of compound 1 along the *a* axis. All H atoms are omitted for clarity. (c, d) Packing representations of 1 along the *a* axis. The lattice water molecules have been omitted for clarity. The atoms with the suffixes A and B are generated by the symmetry operation: A: 0.5 - x, -0.5 - y, -1 - z; B: 1 - x, y, -0.5 - z.



Figure 2. (a) Drawing of the structural unit of **2** with partial atom labeling scheme. The hydrogen atoms and solvent water molecules are omitted for clarity. (b) The π - π stacking diagram of polyoxoanions in **2** along the *a* axis, showing the 1D chain structure. Hydrogen atoms and water molecules were omitted for clarity. The atoms with the suffixes A and B are generated by the symmetry operation: A: -x, 1 - y, -z; B: -1 - x, -y, 1 - z.

The band at 862 cm⁻¹ for 1, 885 cm⁻¹ for 2, 858 cm⁻¹ for 3, 856 cm⁻¹ for 4, and 854 cm⁻¹ for 5 is attributed to the ν (Nb–O_t) bond. The vibration resonance in 400–800 cm⁻¹ is assigned to the ν (Nb–O_b–Nb) bond.^{2e} In addition, the occurrence of characteristic vibrations between 1440–1490 cm⁻¹ and 1430–1520 cm⁻¹ confirms the presence of 2,2'-bipy and phen ligands.^{31,32}

UV spectra in the aqueous solution displays two absorption bands at approximately 243 and 296 nm for 1, 225 and 269 nm for 3, 227 and 269 nm for 4, 225 and 270 nm for 5, respectively (Figure S3, Supporting Information), which can be tentatively assigned to the $p\pi$ -d π charge-transfer transitions of O \rightarrow Nb bonds.²¹

Thermogravimetric (TG) Analyses. The TG properties of 1-5 were measured under air atmosphere with a heating rate of 10 °C·min⁻¹ from 25 to 800 °C (Figure S4, Supporting Information). The TG curves of 1 indicate two-step weight loss, while the weight loss of 2-5 can be divided into multiple steps.



Figure 3. (a) Drawing of the asymmetric unit of complex 3 with partial atom labeling scheme. The hydrogen atoms and solvent water molecules are omitted for clarity. (b) The π - π stacking diagram of polyoxoanions in 3 along the *c* axis, showing the 1D chain structure. Hydrogen atoms and water molecules were omitted for clarity. The atoms with the suffixes A are generated by the symmetry operation: A: 1.5 - x, 0.5 - y, -z.

For 1, the total weight loss is 39.57% in the range of 25-800 °C (calcd. 38.52%). The first weight loss is 1.95% from 25 to 100 °C, assigned to the release of two lattice water molecules (calcd. 1.43%), followed by the loss of 37.62% corresponding to the removal of six 2,2'-bipy ligands (calcd. 37.09%) from 100 to 800 °C. For 2, the total weight loss is 46.30% in the range of 25-800 °C (calcd. 44.53%). The weight loss of 6.34% during the first step from 25 to 108 °C corresponds to the release of eight and a half lattice water molecules (calcd. 5.47%). On further heating, the second weight loss of 22.96% between 108-490 °C is approximately attributed to the removal of four 2,2'-bipy ligands (calcd. 22.32%). The third weight loss of 17.00% up to 800 $^{\circ}$ C is ascribed to the removal of three 2,2'-bipy ligands (calcd. 16.74%). As for 3, the TG curve gives a total loss of 48.63% in the range of 25-800 °C (calcd. 47.50%). The weight loss of 5.22% during the first step from 25 to 120 °C involves the loss of eight lattice water molecules (calcd. 4.87%). On further heating, the sample loses weight continuously during the second step with the weight loss of 37.09% from 120 to 551 °C corresponding to the removal of six phen ligands (calcd. 36.54%). A following weight loss of 6.32% approximately between 551-800 °C corresponds to the removal of one phen ligand (calcd. 6.09%). For 4, the total loss is 48.08% in the range of 25-800 °C (calcd. 47.19%). The first weight loss is 5.07% from 25 to 122 °C, assigned to the release of eight lattice water molecules (calcd. 4.84%), followed by the loss of 11.39% approximating the removal of two phen ligands from 122 to 395 °C (calcd. 12.10%). The third weight loss of 25.13% from 395 to 578 $^{\circ}\mathrm{C}$ results from the release of four phen ligands (calcd. 24.20%). After 578 °C, the weight loss of 6.49% (calcd. 6.05%) until 800 °C is observed and assigned to the removal of one phen ligand. For 5, the TG curve gives a total loss of 48.88% in the range of 25-800 °C (calcd. 47.52%). The first weight loss of 5.37% between 25-119 °C corresponds to the release of eight lattice water molecules (calcd. 4.87%). The weight loss of 6.60% during the second step from 119 to 436 °C corresponds to the removal of one phen ligand (calcd. 6.10%). On further heating, the materials lose weight continuously during the third step with the weight loss of 30.57% from 436 to 580 °C corresponding to the release of five phen ligands (calcd. 30.45%). The fourth weight loss of 6.34% from 580 to 800 °C involves the loss of one phen ligand (calcd. 6.10%). These observations indicate the experimental values are approximately consistent with the theoretical values.

Photoluminescence. Organic-inorganic hybrid materials have been developed for fluorescence properties and potential applications in lighting, lasers, and analytical probes.³³ Therefore, the photoluminescence properties of 1 and 3-5 were investigated in polycrystalline powders scattered on a plate intersecting with incidence at an angle of 45°. Upon excitation with 363 nm, 1 shows an intense emission band at ca. 467 nm (Figure 4a), which is attributed to the combined interaction of intraligand $\pi - \pi^*$ transitions and ligand-to-metal-charge-transfer (LMCT) transitions. In comparison with free 2,2'-bipy, ³² the emission band in 1 exhibits a remarkable red-shift of 107 nm, which may originate from coordination of 2,2'-bipy to the nickel center.^{34,35} Upon excitation of 3 and 5 at 365 and 346 nm, respectively, an intense band is observed at 467 nm for 3 (Figure 4b) and 450 nm for 5 (Figure 4d). To understand the nature of the emission bands, we also investigated the luminescence of the free phen, and two intense emission bands centered at 362 and 380 nm occurred (Figure S5, Supporting Information). Thus, we propose the origin of emission of 3 and 5 from a common interaction of the intraligand $\pi - \pi^*$ transitions and LMCT transitions. In comparison with the free phen, the red-shift of the emission bands in 3 and 5 are mainly due to the coordination effect.^{35,36} When excited at 340 nm, 4 shows a main band at 382 nm with a shoulder at about 402 nm, which can be ascribed to the LMCT transitions as well as the intraligand $\pi - \pi^*$ transitions.^{36,37}

EPR Spectra. X-band EPR spectra of polycrystalline powders of 5 were recorded at room temperature and 110 K (Figure 5). The results indicate that the Co^{II} ions are in high-spin state with three unpaired electrons. However, the spectroscopic complexity of high-spin Co^{II} ions with respect to the orbital degeneracy of the ground state and coupling of excited-state terms with changes in coordination environment permits only a qualitative characterization. In order to understand the EPR spectra, consider the term-splitting diagram for high-spin Co^{II} ions in crystal fields of different symmetry. The influence of the crystal-field and the spin-orbit coupling of transition-metal ions is previously discussed.³⁸ Splitting of spectroscopic states of high-spin Co^{f1} ions in coordination compounds leads to two general patterns which is originated from the combined effects of the symmetry of the crystal-field and the spin—orbit coupling.³⁹ They correspond to a high-spin d⁷ configuration either in an orbitally nondegenerate ground state (⁴A₂) or in an orbitally degenerate ground state $({}^{4}T_{1})$, in which the orbital levels are separated by the spin-orbit coupling. At room temperature, the Co^{II} ions tend to populate



Figure 4. Photoluminescence spectra of 1 (a), 3 (b), 4 (c), and 5 (d) at room temperature.

 $M_{\rm s} = \pm 3/2$ level, which is not EPR-active; thus, the EPR signals are almost undetectable. When the systems are cooled to 110 K, the resolution improves considerably, as a result of the signal narrowing induced apparently by the increasing spin—lattice relaxation time. The spectrum displays a very broad band



Figure 5. The EPR spectra of 5 recorded at 110 K and 300 K.

centered at an effective *g* value of 2.09 with a very weak but distinct hyperfine splitting pattern resulting from the interaction of the unpaired electron with the ⁵⁹Co nucleus (I = 7/2), and two narrow symmetric bands centered at effective *g* values of 4.28 and 7.06 that are assigned to the characteristics of high-spin Co^{II} ions. These effective *g* values are very close to those previously reported studies where Co^{II} ions are present at octahedral lattice sites.⁴⁰⁻⁴² In addition, when the temperature decreases to 110 K, the EPR signals centered at an average g = 4.28 and 7.06 become stronger, probably due to the zero-field splitting effect.⁴² Therefore, the EPR spectra of **5** suggest that the Co^{II} ions are in octahedral environments.

CONCLUSIONS

Five new organic-inorganic hybrid PONs [Ni(2,2'-bipy)₂]₃- $[Nb_{10}O_{28}] \cdot 2H_2O$ (1), $[Ni(2,2'-bipy)_3] \{ [Ni(2,2'-bipy)_2]_2 -$ $[Nb_{10}O_{28}]$ + 8.5H₂O (2), $[M(phen)_3]{[M(phen)_2]_2}$ $[Nb_{10}O_{28}]$ + 8H₂O (M = Ni for 3; M = Zn for 4; M = Co for 5) have been harvested under hydrothermal conditions. 1 is the first 1D chain architecture built by [Nb₁₀O₂₈]⁶⁻ units and $[Ni(2,2'-bipy)_2]_3^{6+}$ cations. Furthermore, adjacent chains in 1 are further interacted by $\pi - \pi$ stacking interactions resulting in a 3D supramolecular network. 2-5 are constructed from $[Nb_{10}O_{28}]^{6-}$ units and different transition-metal complexes. Neighboring units in 2–5 are combined together via the π - π interactions between pyridine rings of ligands forming a 1D linear supramolecular chain. As far as we know, 1-3 are the first examples of organic-inorganic hybrid nickel-containing decaniobates. The phenomenon that the $[Nb_6O_{19}]^{8-}$ precursor transformed to the $[Nb_{10}O_{28}]^{6-}$ cluster was observed in 1–5. Furthermore, the successful preparations of 1-5 enrich the structural diversity of decaniobate compounds and provide us with an enlightening synthetic strategy for the introduction of other transition-metal or aromatic ligands into the $[Nb_{10}O_{28}]^6$ cluster to construct novel organic-inorganic hybrid PONs. In the following exploration, we will continue to investigate the pertinent synthetic chemistry. Moreover, the exploration of $[Nb_6O_{19}]^{8-}$ precursors to accommodate other transition-metal or rare-earth cations and organic ligands through hydrothermal method is in progress.

ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic files for 1-5 in CIF format and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jyniu@henu.edu.cn, jpwang@henu.edu.cn. Fax: (+86) 378 3886876.

ACKNOWLEDGMENT

This work was supported by the Natural Science Foundation of China, Special Research Fund for the Doctoral Program of Higher Education, Innovation Scientists and Technicians Troop Construction Projects of Henan Province, the Foundation of Education Department of Henan Province and Natural Science Foundation of Henan Province.

REFERENCES

(1) (a) Hill, C. L. J. Mol. Catal. A 2007, 262, 2–6. (b) Coronado, E. C.; Gimenez-Saiz, C.; Gomez-Garcia, J. Coord. Chem. Rev. 2005, 249, 1776–1796. (c) Hasenknopf, B. Front. Biosci. 2005, 10, 275–287. (d) Long, D. L.; Burkholder, E.; Cronin, L. Chem. Soc. Rev. 2007, 36, 105–121. (e) Pope, M. T.; Müller, A. Angew. Chem. 1991, 103, 56–70.

(2) (a) Rhule, J. T.; Hill, C. L.; Judd, D. A. Chem. Rev. 1998, 98, 327–358. (b) Cjoamg, M. H.; Williams, C. W.; Soderhlm, L.; Antonio, M. R. Eur. J. Inorg. Chem. 2003, 14, 2663–2669. (c) Russell, A. J.; Berberich, J. A.; Drevon, G. F.; Koepsel, R. R. Annu. Rev. Biomed. Eng. 2003, 5, 1–27. (d) Kortz, U.; Savelieff, M. G.; Bassil, B. S.; Keita, B.; Nadjo, L. Inorg. Chem. 2002, 41, 783–789. (e) Besserguenew, A.; Dickman, M.; Pope, M. Inorg. Chem. 2001, 40, 2582–2586. (f) Bonhomme, F.; Larentzos, J. P.; Alam, T. M.; Maginn, E. J.; Nyman, M. Inorg. Chem. 2005, 44, 1774–1785. (g) Ohlin, C. A.; Villa, E. M.; Fettinger, J. C.; Casey, W. H. Angew. Chem., Int. Ed. 2008, 47, 5634–5636. (h) Kim, G.-S.; Zeng, H.; Neiwert, W. A.; Cowan, J. J.; VanDerveer, D.; Hill, Craig. L.; Weinstock, Ira. A. Inorg. Chem. 2003, 42, 5537–5544.

(3) (a) Wassermann, K.; Dickman, M. H.; Pope, M. T. Angew. Chem., Int. Ed. 1997, 36, 1445–1448. (b) Müller, A. P.; Kuhlmann, K. C. Chem. Commun. 1999, 15, 1347–1358. (c) Müller, A.; Rohlfing, R.; Döring, J.; Penk, M. Angew. Chem., Int. Ed. 1991, 30, 588–590.

(4) Lindqvist, I. Ark. Kemi 1953, 5, 247-250.

(5) Flynn, C. M.; Stucky, G. D. Inorg. Chem. 1969, 8, 332-335.

(6) Graeber, E. J.; Morosin, B. Acta Crystallogr. Sect. 1977, B33, 2137–2143.

(7) Yamase, T.; Naruke, H.; Sasaki, Y. Inorg. Chem. 1994, 33, 409-410.

(8) Besserguenew, A.; Dickman, M.; Pope, M. Inorg. Chem. 2001, 40, 2582–2586.

(9) Nyman, M.; Bonhomme, F.; Alam, T. M.; Rodriguez, M. A.; Cherry, B. R.; Krumhansl, J. L.; Nenoff, T. M.; Sattler, A. M. *Science* **2002**, 297, 996–998.

(10) Nyman, M.; Bonhomme, F.; Alam, T. M.; Parise, J. B.; Vaughan, G. M. B. Angew. Chem., Int. Ed. **2004**, 43, 2787–2792.

(11) Nyman, M.; Celestian, A. J.; Parise, J. B.; Holland, G. P.; Alam,
 T. M. *Inorg. Chem.* 2006, 45, 1043–1052.

(12) Maekawa, M.; Ozawa, Y.; Yagasaki, A. Inorg. Chem. 2006, 45, 9608–9609.

(13) Bontchev, R. P.; Nyman, M. Angew. Chem., Int. Ed. 2006, 45, 6670–6672.

(14) Bontchev, R. P.; Venturini, E. L.; Nyman, M. Inorg. Chem. 2007, 46, 4483–4491.

(15) Shen, L.; Li, C. H.; Chi, Y. N.; Hu, C. W. Inorg. Chem. Commun. 2008, 11, 992–994.

(16) Villa, E. M.; Ohlin, C. A.; Balogh, E.; Anderson, T. M.; Nyman,
 M. D.; Casey, W. H. Angew. Chem., Int. Ed. 2008, 47, 4844–4846.

(17) Tsunashima, R.; Long, D. L.; Miras, H. N.; Gabb, D.; Pradeep, C. P.; Cronin, L. Angew. Chem., Int. Ed. **2009**, 48, 113–117.

(18) Niu, J. Y.; Ma, P. T.; Niu, H. Y.; Li, J.; Zhao, J. W.; Song, Y.; Wang, J. P. *Chem.*—*Eur. J.* **2007**, *13*, 8739–8748.

(19) Wang, J. P.; Niu, H. Y.; Niu, J. Y. Inorg. Chem. Commun. 2008, 11, 63–65.

(20) (a) Gao, Y.; Twamley, B.; Shreeve, J. M. Organometallics. 2006, 25, 3364–3369. (b) Du, M.; Zhang, Z. H.; Zhao, X. J. Cryst. Growth Des. 2006, 6, 114–121. (c) Dong, Y. B.; Smith, M. D.; Loye, H. C. Inorg. Chem. 2000, 39, 4927–4935.

(21) Niu, J. Y.; Chen, G.; Zhao, J. W.; Ma, P. T.; Li, S. Z.; Wang, J. P.; Li, M. X.; Bai, Y.; Ji, B. S. *Chem.—Eur. J.* **2010**, *16*, 7082–7086.

(22) Niu, J. Y.; Fu, X.; Zhao, J. W.; Li, S. Z.; Ma, P. T.; Wang, J. P. Cryst. Growth Des. **2010**, *10*, 3110–3119.

(23) Filowitz, M.; Ho, R. K. C.; Klemperer, W. G.; Shum, W. Inorg. Chem. 1979, 18, 93-103.

(24) (a) Sheldrick, G. M. SHELXS-97, Program for Crystal Structure Solution; University of Göttingen: Göttingen, Germany, 1997. (b) Sheldrick, G. M. SHELXL-97, Program for Crystal Structure Refinement; University of Göttingen: Germany, 1997.

(25) Anderson, T. M.; Thoma, S. G.; Bonhomme, F.; Rodriguez, M. A.; Park, H.; Parise, J. B.; Alam, T. M.; Larentzos, J. P.; Nyman, M. *Cryst. Growth. Des.* **2007**, *7*, 719–723.

(26) Laurencin, D.; Thouvenot, R.; Boubekeur, K.; Proust, A. Dalton Trans. 2007, 1334–1345.

(27) (a) Hegetschweiler, K.; Finn, R. C.; Rarig, J. R. S.; Sander, J.; Steinhauser, S.; Wörle, M.; Zubieta, J. *Inorg. Chim. Acta* **2002**, *337*, 39– 47. (b) Chen, S. M.; Zhang, J.; Lu, C. Z. *CrystEngComm* **2007**, *9*, 390– 393. (c) Zhang, Z. M.; Li, Y. G.; Yao, S.; Wang, E. B.; Wang, Y. H.; Clérac, R. *Angew. Chem., Int. Ed.* **2009**, *48*, 1581–1584. (d) Zhao, J. W.; Shi, D. Y.; Chen, H. L.; Chen, L. J.; Ma, P. T.; Niu, J. Y. *Inorg. Chem. Commun.* **2010**, *13*, 822–827.

(28) Zheng, L. M.; Wang, Y. S.; Wang, X. Q.; Korp, J. D.; Jacobson, A. J. *Inorg. Chem.* **2001**, *40*, 1380–1385.

(29) (a) Niu, J. Y.; Guo, D. J.; Wang, J. P.; Zhao, J. Y. *Cryst. Growth Des.* **2004**, *4*, 241–247. (b) Dai, L. M.; You, W. S.; Wang, E. B.; Wu, S. X.; Su, Z. M.; Du, Q. H.; Zhao, Y.; Fang, Y. *Cryst. Growth Des.* **2009**, *9*, 2110–2116.

(30) Wang, J. P.; Zhao, J. W.; Li, S. Z.; Niu, J. Y. J. Coord. Chem. 2006, 59, 597–605.

(31) (a) Zhao, J. W.; Wang, C. M.; Zhang, J.; Zheng, S. T.; Yang, G. Y. *Chem.—Eur. J.* 2008, *14*, 9223–9239. (b) Yuan, M.; Li, Y. G.; Wang, E. B.; Tian, C. G.; Wang, L.; Hu, C. W.; Hu, N. H.; Jia, H. Q. *Inorg. Chem.* 2003, *42*, 3670–3676.

(32) Sun, C. Y.; Li, Y. G.; Wang, E. B.; Xiao, D. R.; An, H. Y.; Xu, L. Inorg. Chem. 2007, 46, 1563–1574.

(33) (a) Würthner, F.; Sautter, A. *Chem. Commun.* **2000**, 445. (b) Ciurtin, D. M.; Pschirer, N. G.; Smith, M. D.; Bunz, U. H. F.; zur Loye, H. C. *Chem. Mater.* **2001**, *13*, 2743–2745. (c) Tao, J.; Shi, J. X.; Tong,

M. L.; Zhang, X. X.; Chen, X. M. Inorg. Chem. 2001, 40, 6328–6330.
 (34) Zhang, L. Y.; Liu, G. F.; Zheng, S. L.; Ye, B. H.; Zhang, X. M.;

Chen, X. M. Eur. J. Inorg. Chem. 2003, 2965–2971.

(35) Yersin, H., Vogler, A., Eds.; *Photochemistry and Photophysics of Coordination Compounds*; Springer: Berlin, 1987.

(36) Hu, X.; Guo, J. X.; Liu, C.; Zen, H.; Wang, Y. J.; Du, W. J. Inorg. Chim. Acta **2009**, 362, 3421–3426.

(37) Zheng, S. L.; Yang, J. H.; Yu, X. L.; Chen, X. M.; Wong, W. T. Inorg. Chem. **2004**, 43, 830–838.

(38) Griffith, J. S. *The Theory of Transition-Metal Ions*; Cambridge University Press: London, 1961.

(39) Carlin, R. L.; von Duyneveldt, A. J. Magnetic Properties of Transition-Metal Compounds; Springer: New York, 1977.

(40) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance of Transitions Ions*; Clarendon Press: Oxford, 1970.

(41) Jankovics, H.; Daskalakis, M.; Raptopoulou, C. P.; Terzis, A.; Tangoulis, V.; Giapintzakis, J.; Kiss, T.; Salifoglou, A. *Inorg. Chem.* **2002**, *41*, 3366–3374.

(42) Wang, J. P.; Ma, P. T.; Li, J.; Niu, H. Y.; Niu, J. Y. Chem. Asian J. 2008, 3, 822–833.

1261