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Ying Zhang, Ai-Quan Jia, Jing-Jing Zhang, Zhifeng Xin, Qian-Feng Zhang

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Construction of {Mn[Ph₂P(O)NP(O)Ph₂]₂} units with mono- and bi-pyridines: syntheses, molecular structures, and spectroscopic properties of manganese(II) complexes with tetraphenylimidodiphosphinates

Ying Zhang, Ai-Quan Jia*, Jing-Jing Zhang, Zhifeng Xin, and Qian-Feng Zhang*

Institute of Molecular Engineering and Applied Chemistry, Anhui University of Technology, Ma'anshan, Anhui 243002, P. R. China

Abstract

Treatment of $[Mn(CH_3COO)_2 \cdot 4H_2O]$ with two equivalents of $K[N(Ph_2PO)_2]$ in the presence of two equivalents of pyridine (py) or 4-^tBu-pyridine (4-^tBu-py) in MeOH-H₂O afforded mononuclear complexes $[Mn{N(Ph_2PO)_2}_2(py)_2]\cdot 2H_2O$ (1) and $[Mn{N(Ph_2PO)_2}_2(4-^tBu-py)_2]$ (2), respectively. Interaction of $[Mn(CH_3COO)_2 \cdot 4H_2O]$ with two equivalents of $K[N(Ph_2PO)_2]$ in the presence of one equivalent of rigid dipyridyl-based ligand 4,4'-bipyridine (bpy) or trans-1,4-bis-(pyridyl)ethene (bpe) resulted in formation of one-dimensional linear polymeric chains $[Mn{N(Ph_2PO)_2}_2(\mu-bpy)]_n$ (3) and $[Mn{N(Ph_2PO)_2}_2(\mu-bpe)\cdot 2CH_2Cl_2]_n$ (5), respectively. Reaction of [Mn(CH₃COO)₂·4H₂O] with each of one equivalent of K[N(Ph₂PO)₂] and K[Ph₂PO₂] in the presence of one equivalent of bpy afforded a polymeric complex $[Mn{N(Ph_2PO)_2}_2(\mu-bpy)]_n$ - $[Mn_2{N(Ph_2PO)_2}_2(\mu-Ph_2PO_2)_2(\mu-bpy)]_n$ (4) which contains two independent one-dimensional linear polymeric chains. Self-assembly reaction of [Mn(CH₃COO)₂·4H₂O], K[N(Ph₂PO)₂], bpy and bpe in a 1:2:1:1 ratio gave a dinuclear complex $[Mn(bpe){N(Ph_2PO)_2}_2]_2(\mu-bpy) \cdot H_2O$ (6). Self-assembly reaction of [Mn(CH₃COO)₂·4H₂O], K[N(Ph₂PO)₂], and a flexible dipyridyl-based ligand 4,4'-trimethylenedipyridine (tmpy) in a 1:2:1 ratio gave a tetranuclear complex $[Mn{N(Ph_2PO)_2}_2(\mu-tmpy)]_4 \cdot 2CH_3OH \cdot 3H_2O$ (7). All complexes are air-stable in the solid-state, and were well characterized by electronic, infrared and mass spectroscopies along with thermogravimetric analyses, and their molecular structures have been well established by X-ray crystallography.

Keywords: Manganese(II) complexes; dichalcogenoimidodiphosphinate; bi-pyridine; self-assembly reaction; crystal structure

^{*} Corresponding authors. Tel. & fax.: +0086-555-2311059.

E-mail addresses: zhangqf@ahut.edu.cn (Q.-F. Zhang), jaiquan@ahut.edu.cn (A.-Q. Jia).

Introduction

Manganese complexes with nitrogen- and/or oxygen-containing ligands are attracting considerable interest in recent years in the fields of bioinorganic chemistry [1-3], magnetic materials [4,5] and industrial catalysis [6,7] along with their rich variable structures [8,9]. Generally speaking, the behaviour of these manganese complexes is mainly dependent on the structure and coordination mode of the ligands in addition to the oxidation number of manganese [10]. Various polynuclear manganese complexes with phosphonates or phosphinates ligands have been studied with respect to their structures and magnetic properties [11-14]. A number of tetranuclear oxide-bridged manganese clusters with mixed-valence Mn^{III}/Mn^{IV} and carboxylate ligands are single-molecular magnets (SMM) being capable of the intriguing redox-active property such as the photosynthetic water oxidization [15–18]. A series of manganese(II) coordination polymers generated using simple N,N'-donor spacers with rod-like characteristics, such as 4,4'-bipyridine (bpy), pyrazine and related species, are widely encountered in the realm of crystal engineering [19–24]. In particular, manganese-salan complexes have been widely used as catalysts for alkene epoxidation [25]. Recently, a few manganese(II) complexes with N-polydentate ligands such as terpyridine and tmtacn (tmtacn = N, N', N''-trimethyl-1,4,7-triazacyclo-nonane) have also been found to be active catalysts in various organic oxidation reactions, such as epoxidation of olefins, hydroxylation of saturated and aromatic hydrocarbons, and oxidation of alcohols, by peroxides [26–28]. It has been noted that the π -donating phosphinate ligands are compatible with both hard and soft metal centers. Recently, we have been interested in the use of imidodiphosphinates $[N(R_2PO)_2]^-$ (R = Ph, i-Pr), which are considered to be inorganic analogues of β -diketonates (Chart 1), can form stable complexes with a variety of metals [29,30]. Unlike β -diketonates, imidodiphosphinates are capable of displaying distinct and unique geometries and electronic properties, and extra steric demands of PR₂ groups relative to CR groups will influence their coordination chemistry. Besides, the conformational freedom of the chelating $R_2P(O)NP(O)R_2$ ring provides a versatile geometric flexibility to the metal complexes. Although many of the reported complexes of these anions are homoleptic tris- and bis-chelate, there still are a growing number of imidodiphosphinato metal complexes with ancillary ligands [31-33]. Only molecular structures of monomeric $[Mn{N(Ph_2PO)_2}_3]$ [34] and dimeric $[Mn{N(Ph_2PO)_2}_2]_2$ [35], which exhibit octahedral {MnO₆} and trigonal bipyramidal {MnO₅}, respectively, have been reported to date. However, manganese(II) complexes with the $\{MnN_2O_4\}$ octahedral coordination sphere containing the chelating imidodiphosphinates and the simple N,N-donor ligands are rare and remain largely unexplored. Rudler and co-workers reported that silver(I)- and copper(II)-[N(Ph₂PO)₂] complexes can catalyze aerobic co-oxidation of hydrocarbons and aldehydes, demonstrating that [N(Ph₂PO)₂]⁻

is stable toward oxidants and thus may find applications in organic oxidations [36]. This prompted us to investigate the syntheses of manganese(II)- $[N(Ph_2PO)_2]$ complexes with pyridine-type compounds. Herein we describe the synthesis, crystal structures, and spectrascopic properties of a series of new manganese(II) complexes with imidodiphosphinato ligands in this paper.

Experimental Section

Materials and Measurements: All syntheses were performed in oven-dried glassware under a purified nitrogen atmosphere using standard Schlenk techniques. The solvents were purified by conventional methods and degassed prior to use. K[N(Ph₂PO)₂] were prepared by the literature methods [37]. Ph₂PO₂K was obtained from the hydrolysis of Ph₂PCl in the lM potassium hydroxide aqueous solution in the presence of H₂O₂. 4,4'-Bipyridine (bpy), *trans*-1,4-bis-(pyridyl)ethene (bpe), 4,4'-trimethylenedi- pyridine (tmpy), Ph₂PCl, and [Mn(CH₃COO)₂·4H₂O] were purchased from Alfa Aesar and used without further purification. All elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer. Electronic absorption spectra were obtained on a Shimadzu UV-3000 spectrophotometer. Infrared spectra were recorded in KBr pellets on a Perkin-Elmer 16 PC FTIR spectrophotometer. Positive FAB mass spectra were recorded on a Finnigan TSQ 7000 spectrometer. The magnetic susceptibilities were measured at 300 K using a Magway MSB Mk 1 magnetic susceptibility balance made by Sherwood Scientific Ltd. Thermogravimetric analysis (TGA) was performed by using a Delta TGA instrument.

Syntheses of Manganese(II) Complexes 1-7

[Mn{N(Ph₂PO)₂}₂(py)₂]·2H₂O (1): To a solution of [Mn(CH₃COO)₂·4H₂O] (25 mg, 0.10 mmol) in MeOH-H₂O (v:v=1:1) (10 mL) was added K[N(Ph₂PO)₂] (92 mg, 0.20 mmol) and pyridine (16 mg, 0.20 mmol) with stirring. The mixture was stirred at room temperature for 4 h. The precipitates were collected by suction filtration and washed twice with 10 mL portions of methanol. White air-stable solids were further recrystallized from MeOH-CH₂Cl₂ (v:v=1:1) to give pink flake crystals of **1** in four days. Yield: 97 mg (90%). IR (KBr disc, cm⁻¹): ν (P₂N) 1230 (s), ν (PO) 1130 (s), 1100 (s). Anal. Calcd. for C₅₈H₅₀N₄O₄P₄Mn·2(H₂O): C, 64.39; H, 5.03; N, 5.18. Found: C, 64.58; H, 4.92; N, 5.23. MS (FAB): *m/z* 1045 (M⁺), 966 (M⁺ – py), 887 (M⁺ – 2py). μ_{eff} = 5.85 μ_{B} .

 $[Mn{N(Ph_2PO)_2}_2(4-{}^tBu-py)_2]$ (2): To a solution of $[Mn(CH_3COO)_2 \cdot 4H_2O]$ (25 mg, 0.10 mmol) in MeOH-H₂O (v:v=1:1) (10 mL) was added K $[N(Ph_2PO)_2]$ (92 mg, 0.20 mmol) and 4-tert-butyl-pyridine (27 mg, 0.20 mmol) with stirring. The mixture was stirred at room temperature for 4 h. The precipitates were collected by suction filtration and washed twice with 10 mL portions of methanol.

White air-stable solids were further recrystallized from MeOH-CH₂Cl₂ (v:v=1:1) to give colorless flake crystals of **2** in three days. Yield: 100 mg (86%). IR (KBr disc, cm⁻¹): ν (P₂N) 1232 (s), ν (PO) 1128 (s), 1100 (s). Anal. Calcd. for C₆₆H₆₆N₄O₄P₄Mn: C, 68.43; H, 5.75; N, 4.84. Found: C, 68.58; H, 5.82; N, 4.93. MS (FAB): m/z 1157 (M⁺), 1022 (M⁺ – 4-^tBu-py), 887 (M⁺ – 2py). μ_{eff} = 5.86 μ_B .

[Mn{N(Ph₂PO)₂}₂(μ -bpy)]_n (3): To a solution of [Mn(CH₃COO)₂·4H₂O] (25 mg, 0.10 mmol) in MeOH-H₂O (v:v=1:1) (15 mL) was added K[N(Ph₂PO)₂] (92 mg, 0.20 mmol) and 4,4'-bipyridine (16 mg, 0.10 mmol) with stirring. The mixture was stirred at room temperature for 2 h. The precipitates were collected by suction filtration and washed twice with 10 mL portions of methanol. Light yellow air-stable solids were further recrystallized from MeOH-CH₂Cl₂ (v:v=3:1) to give yellow bar crystals of **3** in three days. Yield: 88 mg (85%). IR (KBr disc, cm⁻¹): ν (P₂N) 1238 (s), ν (PO) 1128 (s), 1098 (s). Anal. Calcd. for C₅₈H₄₈N₄O₄P₄Mn: C, 66.72; H, 4.64; N, 5.37. Found: C, 66.88; H, 4.73; N, 5.43. MS (FAB): m/z 1043 (M⁺), 887 (M⁺ – bpy). μ_{eff} = 5.88 μ_{B} .

[Mn{N(Ph₂PO)₂}₂(μ-bpy)]_n[Mn₂{N(Ph₂PO)₂}₂(μ-Ph₂PO₂)₂(μ-bpy)]_n (4): To a solution of [Mn(CH₃COO)₂·4H₂O] (25 mg, 0.10 mmol) in MeOH-H₂O (v:v=1:1) (15 mL) was added K[N(Ph₂PO)₂] (92 mg, 0.10 mmol), Ph₂PO₂K (26 mg, 0.10 mmol) and 4,4'-bipyridine (16 mg, 0.10 mmol) with stirring. The mixture was stirred at room temperature for 2 h. The precipitates were filtered and the mother liquid was evaporated to give light yellow air-stable crystals of **4** in five days. Yield: 39 mg (45%), IR (KBr disc, cm⁻¹): ν (P₂N) 1240 (s), ν (PO) 1128 (s), 1100 (s). Anal. Calcd. for C₁₄₀H₁₁₆N₈O₁₂P₁₀Mn₃: C, 65.23; H, 4.54; N, 4.35. Found: C, 65.38; H, 4.63; N, 4.40. MS (FAB): *m/z* 1376 {Mn₂{N(Ph₂PO)₂}₂(μ-Ph₂PO₂)₂, 887 {Mn{N(Ph₂PO)₂}₂). μ_{eff} = 5.88 μ_B.

[Mn{N(Ph₂PO)₂}₂(μ -bpe)·2CH₂Cl₂]_n (5): To a solution of [Mn(CH₃COO)₂·4H₂O] (25 mg, 0.10 mmol) in MeOH-H₂O (v:v=1:1) (15 mL) was added K[N(Ph₂PO)₂] (92 mg, 0.20 mmol) and *trans*-1,4-bis-(pyridyl)ethene (18 mg, 0.10 mmol) with stirring. The mixture was stirred at room temperature for 4 h. The precipitates were collected by suction filtration and washed twice with 10 mL portions of methanol. Light yellow air-stable solids were further recrystallized from MeOH-CH₂Cl₂ (v:v=3:1) to give yellow bar crystals of **5** in three days. Yield: 112 mg (90%). IR (KBr disc, cm⁻¹): ν (P₂N) 1238 (s), ν (PO) 1126 (s), 1097 (s). Anal. Calcd. for C₆₀H₄₄N₄O₄P₄Cl₄Mn·2(CH₂Cl₂): C, 60.14; H, 4.40; N, 4.53. Found: C, 60.18; H, 4.43; N, 4.48. MS (FAB): m/z 1203 (M⁺), 887 (M⁺ – bpe). μ_{eff} = 5.89 µ_B.

[Mn(bpe){N(Ph₂PO)₂}₂]₂(μ -bpy)·H₂O (6): To a solution of [Mn(CH₃COO)₂·4H₂O] (25 mg, 0.10 mmol) in MeOH-H₂O (v:v=5:1) (15 mL) was added K[N(Ph₂PO)₂] (92 mg, 0.20 mmol), 4,4'-bipyridine (16 mg, 0.10 mmol) and *trans*-1,4-bis-(pyridyl)ethene (18 mg, 0.10 mmol) with stirring. The mixture was stirred at room temperature for 4 h. The precipitates were collected by suction filtration and washed twice with 10 mL portions of methanol. Yellow air-stable solids were further recrystallized from MeOH-CH₂Cl₂ (v:v=2:1) to give yellow block crystals of **6** in three days. Yield: 98 mg (85%). IR (KBr disc, cm⁻¹): ν (P₂N) 1242 (s), ν (PO) 1130 (s), 1100 (s). Anal. Calcd. for C₁₃₀H₁₀₈N₁₀O₈P₈Mn₂·(H₂O): C, 67.46; H, 4.79; N, 6.06. Found: C, 67.58; H, 4.73; N, 6.13. MS (FAB): *m/z* 2294 (M⁺), 2140 (M⁺ – bpy), 887 {Mn{N(Ph₂PO)₂}. μ_{eff} = 5.91 μ_{B} .

[Mn{N(Ph₂PO)₂}₂(μ -tmpy)]₄·2CH₃OH·3H₂O (7): To a solution of [Mn(CH₃COO)₂·4H₂O] (25 mg, 0.10 mmol) in MeOH-H₂O (v:v=5:1) (12 mL) was added K[N(Ph₂PO)₂] (92 mg, 0.20 mmol) and 4,4'-trimethylenedipyridine (12 mg, 0.10 mmol) with stirring. The mixture was stirred at room temperature for 3 h. The precipitates were collected by suction filtration and washed twice with 10 mL portions of methanol. Light yellow air-stable solids were further recrystallized from MeOH-CH₂Cl₂ (v:v=2:1) to give yellow block crystals of **7** in three days. Yield: 100 mg (90%). ν (P₂N) 1242 (s), ν (PO) 1131 (s), 1100 (s). Anal. Calcd. for C₂₄₄H₂₂₂N₁₆O₁₆P₁₆Mn₄·(2CH₄O)·-(3H₂O): C, 66.13; H, 5.32; N, 5.02. Found: C, 66.28; H, 5.37; N, 5.13. MS (FAB): *m/z* 4347 (M⁺), 887 {Mn{N(Ph₂PO)₂}}. μ_{eff} = 5.92 μ_{B} .

X-Ray Crystallography: Crystallographic data and experimental details for $[Mn{N(Ph_2PO)_2}_2(py)_2] \cdot 2H_2O$ (1), $[Mn{N(Ph_2PO)_2}_2(4-^tBu-py)_2]$ (2), $[Mn{N(Ph_2PO)_2}_2(\mu-bpy)]_n$ (3), $[Mn{N(Ph_2PO)_2}_2(\mu-bpy)]_n[Mn_2{N(Ph_2PO)_2}_2(\mu-Ph_2PO_2)_2(\mu-bpy)]_n$ (4), $[Mn{N(Ph_2PO)_2}_2-\mu-bpy]_n$ $(\mu$ -bpe)·2CH₂Cl₂]_n (5), [Mn(bpe){N(Ph₂PO)₂}₂]₂(μ -bpy)·H₂O (6), and [Mn{N(Ph₂PO)₂}₂- $(\mu$ -tmpy)]₄·2CH₃OH·3H₂O (7) are summarized in Table 1, and their selected relevant bond distances and angles are collected in Table 2 for comparison. Intensity data were collected on a Bruker SMART APEX 2000 CCD diffractometer using graphite-monochromated Mo-Kα radiation $(\lambda = 0.71073 \text{ Å})$ at 293(2) K. The collected frames were processed with the software SAINT [38]. The data was corrected for absorption using the program SADABS [39]. Structures were solved by the direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [40]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C_{sp3} -H = 0.96 and C_{sp2} -H = 0.93 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent carbon atoms before the final

cycle of least-squares refinement. The solvent molecules in 7 were isotropically refined without hydrogen atoms due to disorder.

Results and Discussion

Syntheses and Spectroscopic Properties. As shown in Scheme 1, treatment of [Mn(CH₃COO)₂·4H₂O] with two equivalents of K[N(Ph₂PO)₂] in the presence of two equivalents of the mono-pyridines, e.g. pyridine (py) or 4-^tBu-pyridine (4-^tBu-py), in MeOH-H₂O afforded mononuclear complexes $[Mn{N(Ph_2PO)_2}_2(py)_2]\cdot 2H_2O$ (1) and $[Mn{N(Ph_2PO)_2}_2(4-^tBu-py)_2]$ (2), respectively, in relatively high yields. Previously, Carli reported the structures of $trans-[Mn^{III}(acac)_2TBP_2]CIO_4$ and $trans-[Mn^{II}(CF_2)_3TBP_2]^0$ (acac = acetylacetonate, $CF_2 = acetylacetonate$ 4,4-difluoro-1-phenylbutanate-1,3-dione, TBP = $4^{-t}Bu$ -py), which were obtained by interactions of [Mn(acac)₃] or [Mn(CF₂)₃] with 4-tert-butyl-pyridine in acetonitrile and stated that the higher oxidation potential due to the fluorinated ligand stabilizes Mn(II) in the latter complex [41]. Similar reactions in the presence of one equivalent of bidentate pyridines such as 4,4'-bipyridine (bpy) and trans-1,4-bis-(pyridyl)ethene (bpe) resulted in isolation of expected polymeric chains $[Mn{N(Ph_2PO)_2}_2(\mu-bpy)]_n$ (3) and $[Mn{N(Ph_2PO)_2}_2(\mu-bpe)\cdot 2CH_2Cl_2]_n$ (5), respectively. A related one-dimensional infinite coordination chain, $[Mn(acac)_2(\mu-bpy)]_n$, was synthesized by solvothermal method using [Mn(CH₃COO)₂·4H₂O], acacH and bpy at 150 °C [42]. Reactions of [Mn(CH₃COO)₂·4H₂O] with each of one equivalent of K[N(Ph₂PO)₂] and K[Ph₂PO₂] in the presence of one equivalent of bpy afforded a polymeric complex $[Mn{N(Ph_2PO)_2}_2(\mu-bpy)]_n$ - $[Mn_2{N(Ph_2PO)_2}_2(\mu-Ph_2PO_2)_2(\mu-bpy)]_n$ (4) which contains two independent one-dimensional linear polymeric chains. One chain is the isomer of complex 3, the other chain is comprised of bpy bridged dinuclear manganese unit $\{Mn_2\{N(Ph_2PO)_2\}_2(\mu-Ph_2PO_2)_2\}$, in which manganese atoms are five coordinated. Self-assembly reaction of [Mn(CH₃COO)₂·4H₂O], K[N(Ph₂PO)₂], bpy and bpe in a 1:2:1:1 ratio gave a dinuclear complex $[Mn(bpe){N(Ph_2PO)_2}_2]_2(\mu-bpy) \cdot H_2O(6)$. Self-assembly reaction of [Mn(CH₃COO)₂·4H₂O], K[N(Ph₂PO)₂] and 4,4'-trimethylenedi-pyridine (tmpy) in a 1:2:1 ratio gave a tetranuclear macro-ring complex $[Mn{N(Ph_2PO)_2}_2(\mu-tmpy)]_4 \cdot 2CH_3OH \cdot 3H_2O$ (7). Previously, the tmpy bridged dinuclear manganese(II) complex $[Mn(hfac)_2(tmpy)_2](C_6H_6)$ was obtained by assembly reaction of $[Mn(hfac)_2 \cdot 3H_2O]$ and tmpy in the presence of benzene (Hhfac = 1,1,1,5,5,5-hexafluoro-pentane-2,4-dione) [43]. Complexes 1–7 are air-stable both in the solid-state and in solution, and soluble in CH₂Cl₂ and slightly soluble in MeOH and H₂O. The characteristic bands for the dichalcogenoimidodiphosphinate complexes 1-7 were found at around 1240 cm⁻¹ for $v_{as}(P_2N)$, 1130 and 1100 cm⁻¹ for v(PO) in the IR spectra. The FAB⁺ mass spectra of compounds

1–7 exhibit molecular ions corresponding to M^+ , $(M^+ - \text{mono-/bi-pyridine})$ and $\{Mn\{N(Ph_2PO)_2\}_2\}$ with the characteristic isotopic distribution patterns. The effective magnetic moment for complexes 1–7 in the range of 5.85–5.92 μ_B at 300 K is very much consistence with the spin only value (5.92 μ_B) for the high spin Mn^{II} [44].

Crystal Structures. The crystal structures of complexes 1–7 have been established by X-ray crystallography (Figures 1-7), in which the tetraphenylimidodiphosphinato ligands all act as monometallic biconnective (chelating) units, leading to six-membered MnO₂P₂N rings, which are conformation in other manganese planar but exhibit a twisted boat as not tetraphenylimidodiphosphinate complexes [34,35,45]. The Mn–O bond lengths ranging from 2.1007(16) to 2.252(3) Å in complexes 1–7 are compared with those in $[Mn{(OPPh_2)_2N}_2]_2$ dimers (av. 2.123(8) Å) [35], the manganese(III) complex Mn[Ph₂P(O)NP(O)Ph₂]₃ (av. 2.007(3) Å) [34] and the mixed-valence dimanganese complex $[Mn_2(CO)_3{Ph_2P(O)NP(O)Ph_2-\mu-O,O'}_3]$ (2.162(6) Å) [45]. The P–O bond lengths ranging from 1.499(3) to 1.516(2) Å are equivalent as the P–N bonds ranging from 1.573(2) to 1.592(2) Å, these values might be considered of intermediate magnitude between single and double phosphorus-oxygen and phosphorus-nitrogen bonds [34], suggesting some delocalization of π electrons over the OPNPO fragments in complexes 1–7. The endocyclic angles of O(1)–Mn(1)–O(2) are in the range of $89.15(11)^{\circ}$ – $91.67(4)^{\circ}$ in complexes 1–7, which agree well to those in related manganese(III) complexes Mn[Ph₂P(O)NP(O)Ph₂]₃ (89.9(1)°, 91.2(1)° and 90.4(1)°) [34] and $[Mn{(OPPh_2)_2N}_2]_2$ (90.1(3)° and 92.3(3)°) [35]. It is noted that the P-N-P bond angles have a wide range of 123.31(13)°-131.73(9)° in complexes 1-7 due to their different geometrical structures.

Complexes **1** and **2** both crystallize in the monoclinic space group $P_{1/n}$ with symmetric structures, which contain discrete monomeric molecules exhibiting an octahedral MnN₂O₄ core in a spiro-bicyclic NP₂O₂MnO₂P₂N system (see Figures 1 and 2), the two pyridine nitrogen atoms occupy the axial positions. The Mn–N bond lengths in complexes **1** and **2** are 2.3035(16) and 2.3135(17) Å, respectively, with the same N–Mn–N bond angles being 180.0°. Figures 3 and 5 show a perspective view of polymeric complexes **3** and **5**, respectively. Complex **3** crystallizes in the monoclinic space group C2/c while complex **5** crystallizes in the triclinic space group P-1. The {Mn[Ph₂P(O)NP(O)Ph₂]₂} units in complexes **3** and **5** are linked by bi-pyridines to form the one-dimensional linear chains. The Mn–N bond lengths are normal. The N–Mn–N bond angles in complexes **3** and **5** are 180.0° and 179.03(8)°, respectively. The dihedral angles of two pyridyl

groups in bpy are $36.09(10)^{\circ}$ for complex **3** and in bpe $60.04(11)^{\circ}$ for complex **5**. The P–N–P bond angle of $131.73(9)^{\circ}$ in **3** is obviously larger than that in **5** (av. $123.31(13)^{\circ}$).

Complex **4** comprises two separate one-dimension chains (Chain A and Chain B). Chain A is linear and isostructural with complex **3**, while Chain B is zig-zag with $\{Mn_2\{N(Ph_2PO)_2\}_2$ - $(\mu$ -Ph_2PO_2)_2 units linked by bpy. Each manganese atom in Chain B is five coordinated with two oxygen atoms from the $[N(Ph_2PO)_2]^-$ ligand, two oxygen atoms from two bridging $[O_2PPh_2]^$ ligands and one pyridine nitrogen atom. The two $[O_2PPh_2]^-$ ligands bridge two manganese atoms to form an eight-membered $Mn_2O_4P_2$ rings, which was also observed in two Mn_{12} single-molecule magnets [46,47] and the dinuclear manganese complexes $[Mn(\mu-dpp)(5-dmbpy)(NO_3)]_2$ (Hdpp is diphenylphosphinic acid, 5-dmbpy = 5,5'-dimethyl-2,2'-dipyridyl) [48] and $[Mn(L)(bpy)_2]_2(ClO_4)_2$ (LH = diphenyl phosphinic acid) [49]. The observed $Mn\cdots Mn$ separation (4.532 Å) is a little shorter than those in related dinuclear complexes $[Mn(\mu-dpp)(5-dmbpy)(NO_3)]_2$ (4.785 and 4.693 Å) [48] and $Mn(L)(bpy)_2]_2(ClO_4)_2$ (4.650 Å) [49]. The Mn–N bond length in Chain B is 2.354(2) Å, similar to those in Chain A (2.232(2) and 2.239(2) Å). Moreover, the bond lengths and bond angles around manganese atoms in complex **4** are compared with those in the related manganese(II) complexes [46–49].

Complexes **6** and **7** crystallize in the triclinic space group *P*-1 with symmetric structures. In complex **6**, the two { $Mn(bpe){N(Ph_2PO)_2}_2$ } species are bridged by bpy to form a dinuclear manganese species. Each manganese atom in complex **6** is six coordinated with four oxygen atoms from two [$N(Ph_2PO)_2$]⁻ ligands, one pyridine nitrogen atom from bpy and one pyridine nitrogen atom from bpe, leaving the other two nitrogen atoms of bpe units uncoordinated. The N–Mn–N bond angle in complex **6** is 176.54(12)°, similar to those in complexes **1–5**. The dihedral angles of two pyridyl groups in bpe is 46.47(19)° for complex **6**, smaller than that in the bpe bridged polymer **5** (60.04(11)°). In complex **7**, the four { $Mn{N(Ph_2PO)_2}_2$ } fragments are linked by four flexible tmpy units to form a tetranuclear macro-ring manganese species with the N–Mn–N bond angles ranging from 172.38(13)° to 177.74(14)°. The two neighbouring pyridyl groups are almost vertical to each other in the tmpy fragment with the dihedral angle being of 87.82(15)°. The parallelogram structure **7** (dimensions: 11.17 × 12.85 Å, see Figure 7) has the Mn···Mn diagonal lengths of 11.21 and 21.31 Å. The dimension of the parallelogram structure is compared with that in the tmpy bridged dinuclear manganese complex (11.389 Å) [43].

Thermal Analyses of Complexes 3 and 7. Thermogravimetric analysis (TGA) was carried out for complex **3** in nitrogen atmosphere. On the basis of weight percentage of steps in TG curve and weight percentage of various molecular parts with respect to monomeric unit, it has been proposed that the first weight loss of 15% in between 175 °C and 250 °C, is due to the removal of bpy. The second weight loss of 65% in between 375 and 585 °C, is due to the removal of carbon, hydrogen oxygen and nitrogen in tetraphenylimidodiphosphinates, which is similar to that of other related complexes [49]. Further heating of this complex till 1000 °C does not lead to any obvious loss (see Figure 8). Similarly, complex **7** shows first weight loss of 67% in the range 375–575 °C, is due to the removal of the other two tmpy units as well as carbon, hydrogen oxygen and nitrogen in tetraphenylimidodiphosphinate groups. No obvious loss is observed when complex **7** is further heated to 1000 °C (see Figure 9).

In summary, a series of structurally diverse manganese(II) tetraphenylimidodiphosphinate complexes with mono- or bi-pyridine ligands were synthesized and characterized from assembly reaction of [Mn(CH₃COO)₂·4H₂O], K[N(Ph₂PO)₂] and pyridine-type compounds under controlled reaction conditions. The preparation of this family of complexes has expanded the limited number of known manganese complexes that contain tetraphenylimidodiphosphinate ligands. Compared to the analogous acac ligands in complexes *trans*-[Mn^{III}(acac)₂TBP₂]ClO₄ and [Mn^{II}(acac)₂(μ -bpy)]_n [41,42], the $[N(Ph_2PO)_2]^-$ ligands in the presented complexes all coordinated to manganese(II), indicating their good characteristics of π -donating ligands. The tetrameric structure of complex $[Mn{N(Ph_2PO)_2}_2(\mu-tmpy)]_4$ (7) is different from the tmpy bridged dinuclear manganese(II) complex $[Mn(hfac)_2(tmpy)_2](C_6H_6)$ [43], possibly due to the conformational freedom of [N(Ph₂PO)₂] ligands. Moreover, the flexible [N(Ph₂PO)₂]⁻ ligands in the mono-, di, tetra-, and poly-nuclear manganese(II) complexes 1–7 all act as monometallic bi-connective units, leading to six-membered MnO₂P₂N rings which are not planar but exhibit a twisted boat conformation as in other manganese tetraphenylimidodiphosphinate complexes [34,35,45], though they exhibit a wider P-N-P bond angle range (123.31(13)°-131.73(9)°) compared to those in other limited complexes $(123.5^{\circ}-129.6^{\circ})$ [34,35,45]. The $\{Mn[N(Ph_2PO)_2]\}$ employment of rigid dipyridyl-based ligands bpy and bpe resulted in the formation of one-dimensional linear polymeric chains, while adoption of flexible dipyridyl-based ligand tmpy in the reaction afforded a tetranuclear macro-ring manganese species with the two neighbouring pyridyl groups almost vertical to each other. Anyway, the N-Mn-N bond angles in complexes 1-7 are similar (172.38(13)°-180.0°), as a result, the stable {Mn[Ph₂P(O)NP(O)Ph₂]₂} units could be explored to obtain more interesting structures. The catalytic properties of these new manganese(II) complexes

with tetraphenylimidodiphosphinato and/or diphenylphosphinato ligands are underway in our laboratory.

Appendix A. Supplementary data

CCDC 1841695-1841701 contains the supplementary crystallographic data for complexes **1–7**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Table 1. Crystallgraphic Data and Experimental Details for $[Mn\{N(Ph_2PO)_2\}_2(py)_2] \cdot 2H_2O(1), [Mn\{N(Ph_2PO)_2\}_2(4-^tBu-py)_2](2), [Mn\{N(Ph_2PO)_2\}_2(\mu-bpy)]_n$ $(3), [Mn{N(Ph_2PO)_2}_2(\mu-bpy)]_n[Mn_2{N(Ph_2PO)_2}_2(\mu-Ph_2PO_2)_2(\mu-bpy)]_n (4), [Mn{N(Ph_2PO)_2}_2(\mu-bpe) \cdot 2CH_2Cl_2]_n (5), [Mn(bpe){N(Ph_2PO)_2}_2]_2(\mu-bpy) \cdot H_2O(\mu-bpe) \cdot 2CH_2Cl_2]_n (5), [Mn(bpe){N(Ph_2PO)_2}_2]_2(\mu-bpe) \cdot 2CH_2Cl_2]_n (5), [Mn(bpe){N(Ph_2PO)_2}_2(\mu-bpe) \cdot 2CH_2Cl_2]_n (5), [Mn(bpe){N(Ph_2PO)_2}_2(\mu-bpe) \cdot 2CH_2Cl_2]_n (5), [Mn(bpe){N(bpe)_2$ (6), and $[Mn{N(Ph_2PO)_2}_2(\mu-tmpy)]_4 \cdot 2CH_3OH \cdot 3H_2O$ (7)

complex	1	2	3	4	5	6	7		
formula	$C_{58}H_{54}N_4O_6$ -	$C_{66}H_{66}N_4O_4$ -	$C_{58}H_{48}N_4O_4P_4Mn$	$C_{140}H_{116}N_8O_{12}$ -	$C_{62}H_{54}N_4O_4Cl_4-$	$C_{130}H_{110}N_{10}O_{9}$ -	$C_{246}H_{236}N_{16}O_{21}$ -		
	P_4Mn	P ₄ Mn		$P_{10}Mn$	P ₄ Mn	P_8Mn_2	$P_{16}Mn_4$		
fw	1081.87	1158.05	1043.82	2576.93	1239.71	2313.92	4467.79		
<i>a</i> , Å	15.2729(13)	13.5109(18)	19.067(3)	25.2649(19)	11.8897(17)	11.5864(15)	15.440(3)		
b, Å	9.7156(8)	9.7219(12)	11.5921(16)	11.5132(9)	11.9407(17)	14.0011(18)	18.751(4)		
<i>c</i> , Å	18.4331(16)	23.286(3)	24.641(3)	44.989(3)	22.615(3)	19.394(3)	20.863(5)		
α , deg					88.102(2)	73.716(2)	81.939(3)		
β , deg	103.893(1)	91.584(2)	103.740(2)	101.049(1)	89.669(2)	83.655(2)	77.803(3)		
γ, deg					71.522(2)	81.113(2)	76.696(3)		
$V, Å^3$	2655.2(4)	3057.5(7)	5290.5(13)	12843.8(17)	3043.4(8)	2976.2(7)	5718(2)		
Ζ	2	2	4	4	2	1	1		
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic		
space group	$P2_{1}/n$	$P2_{1}/n$	C2/c	C2/c	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1		
$ ho_{\rm calc}, {\rm g \ cm}^{-3}$	1.353	1.258	1.311	1.333	1.353	1.291	1.297		
no. of refln	16003	18426	16058	39286	19033	18531	35847		
no. of indep. refln.	6044	6938	5970	14630	13425	13028	25292		
parameter	339	374	323	782	712	728	1405		
R1, wR2 I>2.0 <i>o</i> (I))	0.0374, 0.0899	0.0409, 0.1138	0.0349, 0.0895	0.0517, 0.1110	0.0504, 0.1257	0.0684, 0.1150	0.0724, 0.1373		
13									
	()								

R1, wR2(all data)0.0533, 0.09850.0589, 0.13100.0467, 0.09710.0871, 0.12490.0725, 0.13950.0967, 0.15600.0979, 0.1741GoF1.0370.9121.0301.0361.0420.9941.011 $R1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2 / \Sigma w|F_o^2|^2]^{1/2}$.GoF = $[\Sigma w(|F_o| - |F_c|)^2 / (N_{obs} - N_{param})]^{1/2}$

Table 2. Comparison of Selected Bond Parameters for Complexes 1–7 (Bond distances in Å and bond angles in deg with esd's in parentheses)

compd.	Mn–O	Mn-N	Р-О	P–N	N-Mn-N	O-Mn-O	P–N–P
1	2.1660(11), 2.1829(12)	2.3035(16)	1.5119(12), 1.5096(13)	1.5875(15), 1.5845(15)	180.0	90.01(4)	129.40(10)
	av. 2.1744(12)		av. 1.5108(13)	av. 1.5860(15)			
2	2.1704(13), 2.1582(14)	2.3135(17)	1.5064(14), 1.5017(14)	1.5824(17), 1.5917(17)	180.0	90.18(5)	127.90(11)
	av. 2.1643(14)		av. 1.5040(14)	av. 1.5870(17)			
3	2.1600(11), 2.1875(11)	2.2578(19), 2.2611(19)	1.5080(11), 1.5069(12)	1.5780(14), 1.5798(14)	180.0	91.67(4)	131.73(9)
	av. 2.1738(11)	av. 2.2594(19)	av. 1.5074(12)	av. 1.5789(14)			
4	2.1007(16)-2.1967(17)	2.232(3)- 2.354(2)	1.5017(18)-1.5059(18)	1.573(2)-1.592(2)	180.000(1)	89.84(6), 90.27(6)	127.89(15), 128.59(15)
	av. 2.1558(17)	av. 2.275(3)	av. 1.5040(18)	av. 1.582(2)		av. 90.06(6)	av. 128.24(15)
5	2.1675(17)-2.2243(17)	2.2841(19)), 2.296(2)	1.5085(18)-1.5157(18)	1.590(2)-1.598(2)	179.03(8)	90.17(6), 89.89(6)	123.46(13), 123.16(13)
	av. 2.1960(17)	av. 2.290(2)	av. 1.5131(18)	av. 1.594(2)		av. 90.03(6)	av. 123.31(13)
6	2.163(3)-2.183(3)	2.304(3), 2.312(3)	1.499(3)-1.510(3)	1.578(3)-1.583(3)	176.54(12)	91.31(10), 90.31(9)	130.0(2), 131.2(2)
	av. 2.169(3)	av. 2.308(3)	av. 1.504(3)	av. 1.581(3)		av. 91.31(10)	av. 130.6(2)
7	2.140(3)- 2.252(3)	2.273(4)- 2.403(4)	1.500(3)-1.512(3)	1.575(4)-1.589(4)	177.74(14), 172.38(13)	86.30(11)-91.62(11)	128.3(2)-131.1(2)
	av. 2.182(3)	av. 2.319(4)	av. 1.504(3)	av. 1.583(4)	av. 175.06(14)	av. 89.15(11)	av. 130.0(2)

Figure Captions:

Chart 1. Structures of imidodiphosphinates and β -diketonates ligands.

Scheme 1. Syntheses of mono-, di-, tetra- and poly-nuclear manganese(II) complexes 1-7.

Figure 1. Structure of $[Mn{N(Ph_2PO)_2}_2(py)_2]\cdot 2H_2O$ 1 with the atom labeling. Thermal ellipsoids have been drawn at the 40% probability level. Hydrogen atoms and solvent molecules are omitted for the clarity.

Figure 2. Structure of $[Mn{N(Ph_2PO)_2}_2(4-{}^tBu-py)_2]$ **2** with the atom labeling. Thermal ellipsoids have been drawn at the 40% probability level. Hydrogen atoms are omitted for the clarity.

Figure 3. A perspective view of one-dimension linear chain of polymeric $[Mn\{N(Ph_2PO)_2\}_2(\mu$ -bpy)]_n **3** with the atom labeling. Thermal ellipsoids have been drawn at the 40% probability level. Hydrogen atoms are omitted for the clarity.

Figure 4. (a) A perspective view of one-dimension linear chain of polymeric $[Mn\{N(Ph_2PO)_2\}_2(\mu$ -bpy)]_n in **4**. Thermal ellipsoids have been drawn at the 40% probability level. Hydrogen atoms are omitted for the clarity. (b) A perspective view of one-dimension zig-zag chain of polymeric $[Mn_2\{N(Ph_2PO)_2\}_2(\mu$ -Ph_2PO_2)_2- $(\mu$ -bpy)]_n in **4**. Thermal ellipsoids have been drawn at the 40% probability level. Hydrogen atoms are omitted for the clarity.

Figure 5. A perspective view of one-dimension chain of polymeric $[Mn\{N(Ph_2PO)_2\}_2(\mu$ -bpe)·2CH₂Cl₂]_n **5** with the atom labeling. Thermal ellipsoids have been drawn at the 40% probability level. Hydrogen atoms and solvent molecules are omitted for the clarity.

Figure 6. Structure of $[Mn(bpe){N(Ph_2PO)_2}_2]_2(\mu$ -bpy)·H₂O **6** with the atom labeling. Thermal ellipsoids have been drawn at the 40% probability level. Hydrogen atoms and solvent molecules are omitted for the clarity.

Figure 7. Structure of $[Mn{N(Ph_2PO)_2}_2(\mu-tmpy)]_4\cdot 2CH_3OH\cdot 3H_2O$ **7** with the atom labeling. Thermal ellipsoids have been drawn at the 40% probability level. Hydrogen atoms and solvent molecules are omitted for the clarity.

Figure 8. TGA trace of $[Mn{N(Ph_2PO)_2}_2(\mu-bpy)]_n$ (3).

Figure 9. TGA trace of $[Mn{N(Ph_2PO)_2}_2(\mu-tmpy)]_4$ (7)

Chart 1.



(i) pyridine or 4-t-Bu-pyridine, MeOH-H₂O; (ii) bpy or bpe, MeOH-H₂O; (iii) bpy, Ph₂PO₂K MeOH-H₂O; (iv) bpy and bpe, MeOH-H₂O; (v) tmpy, MeOH-H₂O

Figure 1.



Figure 3.



Figure 4.



(a)



(b)

Figure 5.



Figure 8.



For Table of Contents

<u>Synopsis</u>

Construction of {Mn[Ph₂P(O)NP(O)Ph₂]₂} units with mono- and bi-pyridines: syntheses, molecular structures, and spectroscopic properties of manganese(II) complexes with tetraphenylimidodiphosphinates

Ying Zhang, Ai-Quan Jia*, Jing-Jing Zhang, Zhifeng Xin, and Qian-Feng Zhang*

Self-assembly reaction of [Mn(CH₃COO)₂·4H₂O], K[N(Ph₂PO)₂] with mono- or bi-pyridines led to construction of mono-, di-, tetra-, and poly-nuclear manganese(II) complexes with tetraphenylimidodiphosphinates under controlled reaction conditions.

