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Cobalt and Manganese Nets via Their Wires: Facile Transformation in Metal–Diorganophosphates

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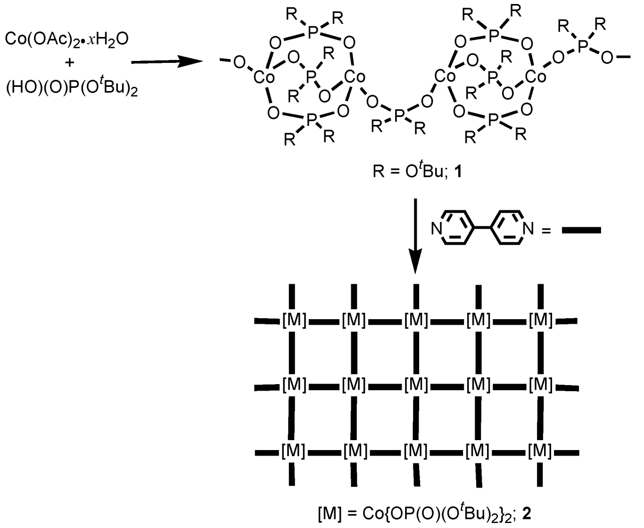
The manganese and cobalt complexes $[M(dtbp)_2]_n$ (M = Mn, Co; dtbp = di-*tert*-butyl phosphate), which exist as one-dimensional molecular wires, transform to $[M(dtbp)_2(bpy)_2 \cdot 2H_2O]_n$ by the addition of 4,4-bipyridine (bpy) at room temperature; the latter compounds form noninterpenetrating rectangular grid structures.

A major interest in metal phosphate chemistry is concerned with the structural transformations under mild conditions.[1] Although it has been suggested by Ozin et al. as early as in 1998 that it is possible to effect transformations among aluminophosphates,[2] only recent experiments have shown that it is indeed possible to convert a molecular aluminophosphate into either a two- or three-dimensional structure.[1] Rao et al. have recently shown that a zero-dimensional zinc phosphate could be transformed to ladder, layer, and three-dimensional structures,[3] apart from its unusual transformation to a sodalite type structure.[4] While a few examples of conversion of low-dimensional molecular phosphates to insoluble crystalline framework solids of higher dimensionality are known,[1] there are no known reports on the transformation of one form of an organic soluble molecular phosphate into another which is also accompanied by a change in the dimensionality. Continuing our interest in organic soluble molecular phosphates,[5,6] we wish to report herein a new one-dimensional organic soluble cobalt−phosphate that can be readily transformed into a two-dimensional grid structure. Reaction of metal acetates with $[(^tBuO)_2P(O)(OH)]$(dtbp-H) at 25 °C results in the formation of tetrameric phosphates $[M_4(dtbp)_6(\mu_4\text{-}O)]$ (M = Zn, Co, Mn).[5a] Addition of strong donor ligands to this reaction breaks these tetramers to monomeric species, while the use of weak Lewis bases leads to the isolation of one-dimensional polymers. Thus, the reaction of cobalt acetate with dtbp-H in the presence of 3,5-dimethylpyrazole (dmp) yields the monomeric $[Co(dmp)_2(dtbp)_2]$;[5a] one-dimensional polymers $[M(dtbp)_2]_n$ (M = Mn or Cu) and $[Cd(dtbp)_2(OH_2)]_n$ are isolated from the same reaction in the presence of very weak Lewis bases.[5b]

In the present study, in an attempt to isolate new structural forms of cobalt−dtbp complexes, we have reacted cobalt acetate with dtbp-H in the presence of the potentially tridentate ligand 1,3-bis(3,5-dimethylpyrazol-1-yl)propan-2-ol. Quite surprisingly, the co-ligand does not coordinate to the metal, and the product isolated is the one-dimensional polymer $[Co(dtbp)_2]_n$ (**1**) (Scheme 1). Compound **1**, which is a new structural form for cobalt−dtbp complexes, has been characterized with the aid of analytical and spectroscopic studies.[7]

Scheme 1. Synthesis of **1** and Its Conversion to **2**



R = O^tBu; **1**

[M] = $Co\{OP(O)(O^tBu)_2\}_2$; **2**

A single crystal X-ray diffraction study[8] reveals that the molecular structure of **1** is similar to $[Mn(dtbp)_2]_n$. Alternat-

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(1) Murugavel, R.; Walawalkar, M. G.; Dan, M.; Roesky, H. W.; Rao, C. N. R. *Acc. Chem. Res.* **2004**, *37*, 763.

(2) Oliver, S.; Kuperman A.; Ozin, G. A. *Angew. Chem., Int. Ed*. **1998**, *37*, 46.

(3) (a) Ayi, A. A.; Choudhury, A.; Natarajan, S.; Neeraj, S.; Rao, C. N. R. *J. Mater. Chem.* **2001**, *11*, 1181. (b) Choudhury, A.; Neeraj, S.; Natarajan, S.; Rao, C. N. R. *J. Mater. Chem.* **2002**, *12*, 1044.

(4) Dan, M.; Udayakumar, D.; Rao, C. N. R. *Chem. Commun.* **2003**, 2212.

(5) (a) Murugavel, R.; Sathiyendiran, M.; Walawalkar, M. G. *Inorg. Chem.* **2001**, *40*, 427. (b) Murugavel, R.; Sathiyendiran, M. *Inorg. Chem*. **2002**, *41*, 6404. (c) Murugavel, R.; Sathiyendiran, M.; Pothiraja, R.; Walawalkar, M. G.; Mallah, T.; Riviére, E. *Inorg. Chem.* **2004**, *43*, 945. (d) Murugavel, R.; Sathiyendiran, M. *Chem. Lett.* **2001**, 84.

(6) Murugavel, R.; Sathiyendiran, M.; Pothiraja, R.; Butcher, R. J. *Chem. Commun.* **2003**, 2546.

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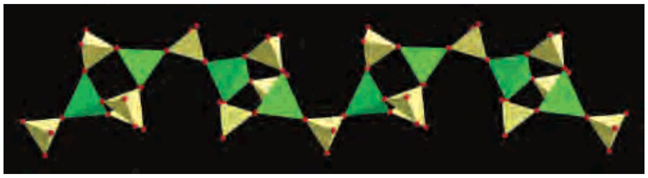

Figure 1. Polyhedral representation of **1** (C and H atoms omitted; green = cobalt, yellow = phosphorus).

ing single and triple phosphate bridges are found between the adjacent Co^{2+} ions in **1**, which are coordinated by four phosphate oxygen atoms in a tetrahedral geometry (O−M−O angles (104.7(1)−116.4(1)°) (Figure 1). The Co−O distances (av 1.956(2) Å) are comparable to the distances reported for other cobalt discrete and extended phosphates.[5a] While the shorter P−O distances are associated with the P−O(M) linkages (av 1.501(2) Å), the longer distances correspond to the P−O(C) linkages (av 1.577(2) Å). The P−O−M angles involving single dtbp bridges are wider (148.2(1)° and 161.6(1)°) compared to the P−O−M angles involving the triple dtbp bridges (131.4(1)−139.5(1)°). These variations are also reflected in the Co···Co distances across the single and triple bridges (3.821(6) and 5.634(7) Å, respectively).

Cobalt polymer **1** transforms readily into a two-dimensional grid structure $[Co(dtbp)_2(bpy)_2{\cdot}(H_2O)_2]_n$ (**2**) by stirring **1** with 2 equiv of bpy in methanol for a few hours (Scheme 1).[9] This transformation is very general, and the manganese polymer $[Mn(dtbp)_2]$ is also transformed to $[Mn(dtbp)_2(bpy)_2{\cdot}(H_2O)_2]_n$ (**3**) under similar conditions in good yields. Compounds **2** and **3** are isomorphous and crystallize with two crystallographically unique metal ions in the asymmetric unit which produce two separate two-dimensional grids. To minimize steric repulsion, these grids are offset from one another; the metal ion in one grid resides centered above the cavity in adjacent grids. The distance between the metal−ligand planes of the two independent adjacent nets is half of the cell length along the *a*-axis (∼7.9 Å).

The metal ions are octahedral and are connected to four 4,4′-bipyridine and two dtbp ligands in *trans* arrangement (Figure 2). The Mn−O bond distances (2.097(2) and 2.124(2) Å) in **2** are similar to those observed for $[Mn(dtbp)_2]_n$.[5a] The Mn···Mn distances along the chain of propagation are 11.72 and 11.86 Å, while the distances across the grid window are 15.51 and 17.76 Å indicating that the grid windows are not rectangular, but parallelepipeds (Figure 3). The size of this void allows incorporation of two water molecules per formula unit of the metal. These water molecules are hydrogen bonded to the phosphoryl oxygens of the phosphate group. The molecular dimensions and the size of the void in cobalt grid **3** are comparable to those of **2**.

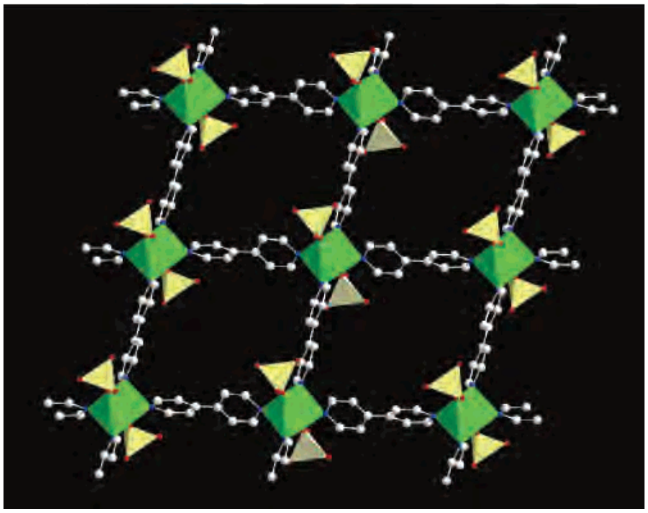

Figure 2. Polyhedral representation of **2** (*tert*-butyl groups and H atoms omitted; green = cobalt, yellow = phosphorus).

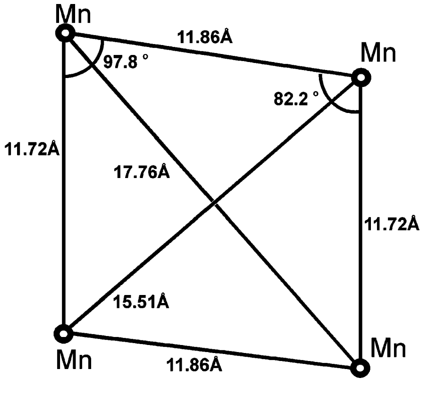

Figure 3. Schematic diagram showing the dimensions of the Mn-grid **3**.

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(7) To $[Co(OAc)_2{\cdot}4H_2O]$ (249 mg, 1 mmol) in methanol (30 mL) were added solid dtbp-H (420 mg, 2 mmol) and 1,3-bis(3,5-dimethylpyrazol-1-yl)propan-2-ol (248 mg, 1 mmol), and the mixture was filtered. The filtrate left for crystallization produced X-ray quality crystals of **1**. Yield: 73%. Anal. Calcd for $C_{16}H_{36}CoO_8P_2$: C 40.3; H 7.6. Found: C 40.0; H 7.6. IR (KBr, cm^{-1}): 2980 (s), 2934 (m), 1486 (m), 1385 (m), 1370 (m), 1252 (m), 1178 (s), 1090 (s), 1076 (vs), 1038 (s), 992 (vs), 916 (m), 841 (m), 709 (m). TGA, temp range °C (% weight loss): 114−152 (47.2); 152−328 (6.4). DSC (°C): 130 (endo); 679 (exo).

(8) Crystal data for **1**: $C_{32}H_{72}Co_2O_{16}P_4$, $M = 954.6$, monoclinic, $P2_1/c$, $Z = 4$, $F(000) = 2024$, $a = 19.940(10)$ Å, $b = 13.286(6)$ Å, $c = 17.739(6)$ Å, $\beta = 90.862(16)°$, $D_c = 1.349$ g cm^{-3}, μ(Mo Kα) = 0.902 mm^{-1}, size = 0.12 × 0.15 × 0.96 mm^3, R1 ($I > 2\sigma(I)$) = 0.0473, $wR_2 = 0.0992$, GOF = 0.999. For **2**: $C_{36}H_{56}CoN_4O_{10}P_2$, $M = 825.7$, monoclinic, $P2/c$, $Z = 4$, $F(000) = 1748$, $a = 15.846(3)$ Å, $b = 11.452(2)$ Å, $c = 23.008(5)$ Å, $\beta = 92.77(3)°$, $D_c = 1.315$ g cm^{-3}, μ(Mo Kα) = 0.545 mm^{-1}, size = 0.4 × 0.2 × 0.2 mm^3, R1 ($I > 2\sigma(I)$) = 0.0954, $wR_2 = 0.2337$, GOF = 1.022. For **3**: $C_{36}H_{56}MnN_4O_{10}P_2$, $M = 821.7$, monoclinic, $P2/c$, $Z = 4$, $F(000) = 1740$, $a = 15.963(1)$ Å, $b = 11.716(1)$ Å, $c = 23.502(2)$ Å, $\beta = 92.783(8)°$, $D_c = 1.243$ g cm^{-3}, μ(Mo Kα) = 0.428 mm^{-1}, size = 0.4 × 0.4 × 0.1 mm^3, R1 ($I > 2\sigma(I)$) = 0.0455, $wR_2 = 0.1301$, GOF = 1.098. The high R1 and wR_2 values obtained for **2** could be attributed to the poor quality of the diffraction data and disordered water molecules in the lattice.

(9) Polymer **1** (1 mmol) was dissolved in methanol (40 mL), and solid 4,4′-bipy (2 mmol) was added and stirred for a few hours to 2 days. The resulting solution was filtered and kept at room temperature to yield **2** as single crystals in 79% yield. Anal. Calcd for $C_{36}H_{56}N_4CoO_{10}P_2$: C 52.4; H 6.8; N 6.8. Found: C 52.1; H 6.5; N 7.6. IR (KBr, cm^{-1}): 3482 (br), 3105 (w), 3081 (m), 2978 (s), 2932 (m), 1604 (s), 1538 (m), 1489 (m), 1414 (m), 1366 (m), 1252 (m), 1197 (s), 1085 (vs), 1037(m), 1008(m), 974 (vs), 823 (m), 705 (m), 629(m), 503(m). TGA, temp range °C (weight loss): 30−96 (4.4); 100−200 (65.0); 200−330 (4.3); 330−700 (8.6). DSC (°C): 50 (endo), 170 (endo); 195 (endo), 340 (endo). Compound **3** was synthesized similarly from $[Mn(dtbp)_2]$. Yield: 63%. Anal. Calcd for $C_{36}H_{56}MnN_4O_{10}P_2$: C 52.6; H 6.9; N 6.8%. Found: C 52.7; H 6.9; N 6.9%. IR (KBr, cm^{-1}): 3493 (vs), 3282 (m), 3078 (m), 2973 (vs), 2927 (s), 1602 (vs), 1537 (s), 1490 (s), 1415 (s), 1391 (s), 1367 (s), 1250 (s), 1221 (s), 1196 (vs), 1081 (s), 1038 (vs), 1008 (vs), 976 (vs), 915 (s), 823 (s), 733 (s), 705 (s). UV−vis (CH_3OH): 296 nm. TGA, temp range °C (% weight loss): 60−100 (4.4); 100−205 (27.3); 205−430 (38.0); 430−600 (4.4). DSC (°C): 107 (endo); 208 (endo).

The presence of *tert*-butoxy groups[10] makes compounds **1**−**3** ideal candidates to produce phosphate materials at low temperatures. The TGA of **1** under N_2 reveals a weight loss of 47% in the range 114−152 °C corresponding to the loss of 4 equiv of *iso*-butene to produce $[Co(O_2P(OH)_2)_2]$. Heating the sample up to 350 °C results in a further weight loss that corresponds to the removal of two water molecules to result in $Co(PO_3)_2$. The TGA traces of both the grid structures **2** and **3** show a similar decomposition behavior. In the case of Mn grid **2**, the first weight loss (∼4.5%) observed between 60 and 110 °C corresponds to the loss of two uncoordinated water molecules. The second weight loss occurs in the range 110−300 °C due to the loss of four *iso*-butene molecules and two 4,4′-bipyridine molecules. The final weight loss corresponds to the loss of two water molecules. The residual mass present in the crucible, after the TGA decomposition under N_2 up to 700 °C, corresponds to the formation of the metaphosphate material. The bulk decomposition of samples **1**−**3** carried out in air at 500 °C for 4 h, however, produced the respective pyrophosphates $M_2P_2O_7$ and not the metaphosphates $M(PO_3)_2$ as evidenced by powder XRD studies. The formation of pyrophosphate is not surprising in view of our recent observation that prolonged heating of copper metaphosphate leads to the release of P_2O_5 and formation of $Cu_2P_2O_7$.[5c] It also appears that elimination of P_2O_5 from metaphosphate materials is facile when the decomposition is carried out in air.

In summary, the formation of a new structural form of cobalt phosphate, $[Co(dtbp)_2]_n$, and its facile conversion to a two-dimensional grid structure have been demonstrated. The non-interpenetrating two-dimensional grid structure for **2** (and **3**) is due to the presence of bulky *tert*-butoxy substituents on phosphate anions, which occupy the axial coordination sites. Molecular grid structures have been recently implicated as useful materials for several applications.[11] In this context, compounds **2** and **3**, with thermally labile organic groups on the axial positions of the metal ions, offer new possibilities. We are presently exploring these aspects.

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Supporting Information Available: Tables of crystal data and refinement parameters, bond lengths and angles, and positional and thermal parameters (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) (a) Lugmair, C. G.; Tilley, T. D.; Rheingold, A. L. *Chem. Mater*. **1997**, *9*, 339. (b) Lugmair, C. G.; Tilley, T. D *Inorg. Chem*. **1998**, *37*, 1821. (c) Lugmair, C. G.; Tilley, T. D.; Rheingold, A. L. *Chem. Mater*. **1999**, *11*, 1615.

(11) Ruben, M.; Rojo, J.; Romero-Salguero, F. J.; Uppadine, L. H.; Lehn, J.-M. *Angew. Chem., Int. Ed*. **2004**, *43*, 3644.