# Di-*tert*-butylphosphate Complexes of Mn(II) and Cu(II) as Single-Source Precursors for Metal Phosphate Materials

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Octahedral Mn(II) and Cu(II) di-*tert*-butylphosphate (L) complexes $[ML_2(imz)_4]$ have been synthesized and characterized using IR, UV-vis, luminescence, and EPR spectroscopy and single crystal X-ray diffraction studies. Thermal decomposition of both the complexes (probed by TGA, DTA, and DSC) indicate stepwise elimination of *iso*-butene, imidazole and water to finally yield the respective ceramic materials $Mn(PO_3)_2$ or $Cu(PO_3)_2$.

Single source precursor approach for the preparation of materials is gaining considerable attention in recent years owing to its ability to provide atomic level control over the composition and homogeneity of the final materials. It has been shown that materials with exceptional properties (e.g. smaller particle size and larger surface area) can be prepared from single source precursors either by sol–gel route or by the simple thermolysis pathway.[1,2] Recent work has shown that the *tert*-butoxy group substituted silanols and phosphorus acids (e.g. $(t\text{-BuO})_2Si(OH)_2$, $(t\text{-BuO})_2P(O)(OH)$, etc.) could be used as starting materials for the preparation of metal complexes which decompose neatly at low temperatures to yield the respective metal silicates or metal phosphates.[3,4] The formation of the ceramic materials proceeds via the elimination of *iso*-butene and water. The use of di-*tert*-butylphosphate, $(t\text{-BuO})_2P(O)(OH)$ (LH) to prepare cage-like and polymeric metal complexes has been demonstrated recently.[3] After thermal decomposition, these di-*tert*-butylphosphate complexes produce a mixture of phosphates (e.g. meta and pyrophosphates) depending on the M:L ratio in these complexes.

In this communication, we wish to describe a simple synthetic route which employs the use of auxiliary ligands to produce mononuclear complexes, $[ML_2(imz)_4]$ (M = Mn (**1**), Cu (**2**), imz = imidazole), and their facile conversion to the metal metaphosphates at fairly low temperatures. Compound **1** was synthesized by adding solid imidazole to a methanol solution of $Mn(OAc)_2{\cdot}4H_2O$ and LH, and leaving the resultant reaction mixture for crystallization.[5] To synthesize **2**, LH was added to a hot methanol solution of $Cu(OAc)_2{\cdot}H_2O$ and stirred for 1 h. The solvent and acetic acid were removed in vacuo and the residue obtained was dissolved in methanol, to which imidazole in THF was added slowly and left for crystallization. After one week, well-formed rectangular single crystals of **2** were obtained.[6]

The IR spectra of both the complexes show strong absorptions at $\nu$ = 973, 1060 and 1220 cm$^{-1}$ for **1** and 977, 1070 and 1208 cm$^{-1}$ for **2**, indicating the presence of both P–O–M and P=O linkages. The absorption maxima for complex **2** was observed at 630 and 300 nm. The former absorption band arises due to the $^2E_g \rightarrow {}^2T_{2g}$ *d–d* transition of octahedral Cu(II).[7] The luminescence excitation and emission spectral studies have been carried out for the Mn(II) complex **1** at both 298 and 77 K. The excitation spectrum exhibits a spectral distribution of bands corresponding to the excited levels of Mn(II) ($^4T_1(^4G)$, 543 nm; $^4A_1$, $^4E(^4G)$, 403 nm; $^4T_2(^4D)$, 374 nm; $^4E(^4D)$, 356 nm), which is accordance to the distribution generally observed for Mn(II) in a octahedral sites.[8]

As expected, the Mn(II) octahedral compound **1** shows a broad EPR signal ($g$ = 2.02). The observance of a broad peak (instead of a sextet) could be ascribed to the increased loading of the solid sample, resulting in the loss of resolution. The EPR spectrum of **2** at room temperature and 77 K shows a signal with a $g$ value 2.01.[9]

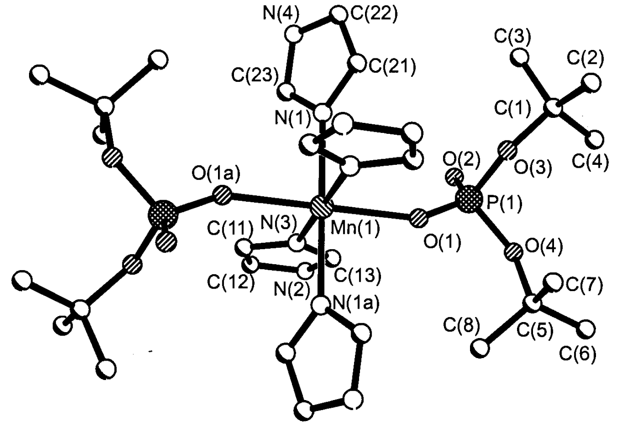

**Figure 1.** Molecular structure of **1**; the structure of **2** is isomorphous.

The solid-state molecular structures of the isostructural compounds **1** and **2** were determined by single crystal X-ray diffraction studies.[10,11] A perspective view of **1** with atom labeling scheme is shown in Figure 1. Selected bond lengths and angles for both **1** and **2** are listed in Table 1. The structure reveals an octahedrally coordinated Mn(II) or Cu(II) ion surrounded by four imidazole molecules in the equatorial positions and two phosphate ligands in the axial positions. The phosphate ligands bind the metal in a unidentate fashion and the P=O functionality is not involved in coordination to the metal. The phosphoryl oxygen, however, forms intermolecular hydrogen bonds to the imidazole N–H groups of the neighboring molecules to result in a tubular structure in the solid state. Other than the M–O and M–N bond distances, there are no larger variations in the metric parameters between **1** and **2**. While the Mn–O distance in **1** is only 2.188(1) Å, the corresponding Cu–O distance in **2** is considerably lengthened due to the Jahn–Teller distortion (2.475(1) Å). Similarly, the equatorial Cu–N distances in **2** (av. 2.025(2) Å) are considerably shorter

**Table 1.** Selected bond lengths [Å] and angles [°] for **1** and **2**

| | M = Mn | M = Cu |
|---|---|---|
| M-O(1) | 2.188(1) | 2.475(1) |
| M-N(1) | 2.243(2) | 2.006(2) |
| M-N(3) | 2.298(2) | 2.045(2) |
| P(1)-O(1) | 1.485(1) | 1.479(1) |
| P(1)-O(2) | 1.498(1) | 1.502(1) |
| P(1)-O(3) | 1.590(1) | 1.598(1) |
| P(1)-O(4) | 1.593(1) | 1.599(1) |
| | | |
| N(1)-M-O(1) | 91.3(1) | 91.2(1) |
| N(1a)-M-O(1) | 88.7(1) | 88.8(1) |
| N(1)-M-N(3) | 90.1(1) | 90.5(1) |
| O(1)-M-N(3) | 91.1(1) | 91.4(1) |
| N(1)-M-N(3a) | 89.9(2) | 89.5(1) |
| O(1)-M-N(3a) | 88.9(1) | 88.7(1) |

than the corresponding Mn–N distances in **1** (av. 2.270(2) Å). The cis and trans L–M–L angles around the metal do not vary much from their ideal values. While the cis angles in **1** are in the range 88.7–91.3°, the observed trans angles are 180°.

In order to demonstrate the utility of compounds **1** and **2** as precursors for phosphate materials, detailed thermal studies have been carried out. The thermogravimetric (TGA) analysis for **1** reveals two distinct weight losses. The major weight loss (66.5%) occurs in between 80 and 325 °C. This weight loss followed by a minor reduction in weight (5%) at 730 °C. The DSC curve show very sharp endotherm at 230 °C corresponding the first weight loss where four *iso*-butene and four imidazole molecules are lost. The second weight loss is due to the loss of two water molecules. The final material obtained is only 28.7% of the initial precursor, which corresponds to the clean formation of $Mn(PO_3)_2$ from **1**. In the thermogravimetric curve for **2** (Figure 2), no weight loss was observed up to 164 °C. The first weight loss observed in TG curve between 164 and 250 °C is assigned to the removal of the *iso*-butene gas and two imidazole molecules. This weight loss causes a strong endothermic peak in DTA curve at 233 °C and strong resolved peaks in DSC at 195 and 210 °C. The second weight loss observed between 250 °C and 650 °C is assigned to the loss of remaining two imidazole and two water molecules. No weight loss was observed after 650 °C; the material left at this temperature (29.4%) matches with the expected theoretical value for the formation of $Cu(PO_3)_2$.

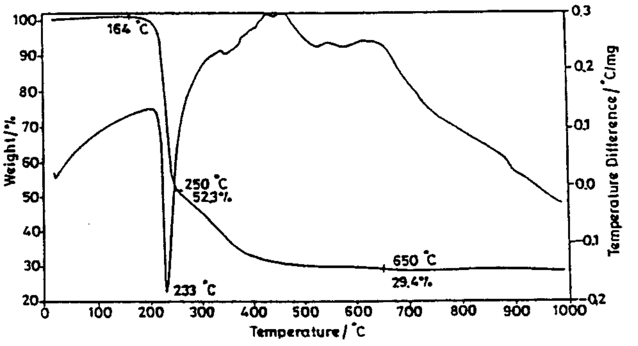

**Figure 2**. TGA and DTA traces of **2** (heating rate 10 °C / min).

To confirm the above observations, the bulk sample of 2 was calcined at 650 °C for ~1 h. However, the XRD pattem of the sample contained amorphous material. Hence, the same sample was again calcined at 700 °C for ~4 h to produce crystalline $Cu(PO_3)_2$.[12] Similarly, the bulk sample of **1** calcined at 700 °C produced an XRD pattern that matches the pattem previously reported for $Mn(PO_3)_2$.[13] These observations indicate that the metaphosphates crystallize around 700 °C.

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5 Spectral data for **1**: Yield: 77'1.. Anal Calcd for $C_{28}H_{52}N_8O_8P_2Mn$ (745.66): C, 45.1; H, 7.0; N, 15.0%.. Found: C, 45.1; H, 6.9; N, 15.2%.. IR (KBr): 3118vs, 3052vs, 2979vs, 2927vs, 286ls, 2710s, 2625s, 1600m, 1544m, 1502m, 1450s, 1365s, 1208s, 1070vs, 977vs, 928s, 830vs, 748vs, 715v, 660vs, 588s, 493s $cm^{-1}$. UV-vis (MeOH): 295 nm. Lum. (MeOH/EtOH): 356, 374, 403, 543 nm.

6 Spectral data for **2**. Yield: 67%.. Anal Calcd for $C_{28}H_{52}N_8O_8P_2Cu$ (754.26): C, 44.6; H, 6.9; N, 14.9%. Found: C, 45.0; H, 6.3; N, 14.7%. IR (KBr): 3112vs, 3032vs, 2973vs, 2933vs, 286ls, 2716s, 2637s, 1600m, 1547m, 1442s, 1362s, 1220vs, 1060vs, 973vs, 912s, 830vs, 75 Ivs, 716vs, 662vs, 584s, 497s $cm^{-1}$. UV-vis (MeOH): 300, 630 nm.

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10 Crystal data for **1**: $C_{28}H_{52}MnN_8O_8P_2$, MW = 745.66, $P\bar{1}$, $a$ = 8.651(1), $b$ = 9.429(1), $c$ = 12.736(1) Å, $\alpha$ = 86.572(6), $\beta$ = 88.398(6), $\gamma$= 67.298(8)°, $U$= 956.7(1) Å$^3$, $D_c$ = 1.294 Mg/m$^3$, Z = 1, F(000) = 395, crystal size = 0.4 × 0.3 × 0.1 mm, $\lambda$ = 0.71073 Å, $\mu$ = 0.482 mm$^{-1}$, $T$ = 293(2) K, $\theta$ range = 1.6 to 25.0°, Final R [$I$>2$\sigma$(I)]: $R_1$ = 0.0296, $wR_2$ = 0.0684, $R$ (all data): $R_1$ = 0.0544, $wR_2$ = 0.0749.

11 Crystal data for **2**: $C_{28}H_{52}CuN_8O_8P_2$, MW = 754.26, $P\bar{1}$, $a$ = 8.362(1), $b$ = 9.308(1), $c$ = 13.030(1) Å, $\alpha$= 87.963(4), $\beta$ = 86.013(4), $\gamma$ = 68.342(5)°, $U$= 940.2(1) Å$^3$, $D_c$ = 1.332 Mg/m$^3$, Z = 1, F(000) = 399, crystal size = 0.5 × 0.35 × 0.2 mm, $\lambda$ = 0.71073 Å, $\mu$ = 0.72 mm$^{-1}$, $T$ = 293(2) K, $\theta$ range = 1.6 to 25.0°, Final $R$ [$I$ > 2$\theta$(I)]: $R_1$ = 0.0280, $wR_2$ = 0.0652, $R$ (all data): $R_1$ = 0.0467, $wR_2$ = 0.0707.

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