Electronic Supplementary Information for

Seeking tetrameric transition metal phosphonate with a D4R core and Organising it into a 3-D supramolecular assembly

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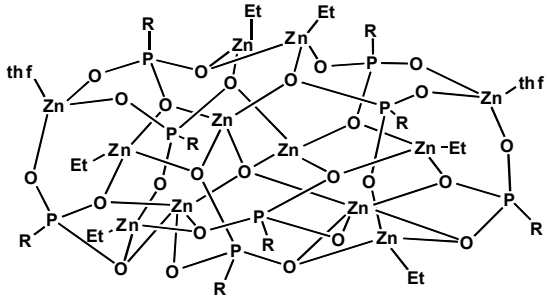
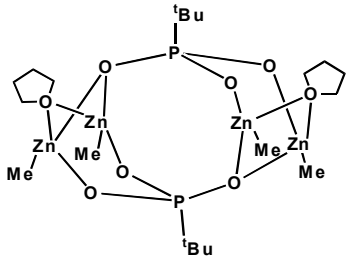
Journal: Chemical Communications



R = ^{t}Bu; Ref. 1



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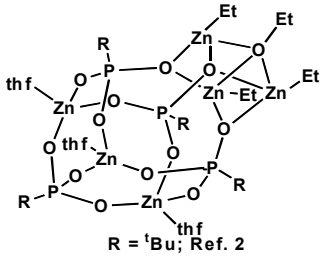

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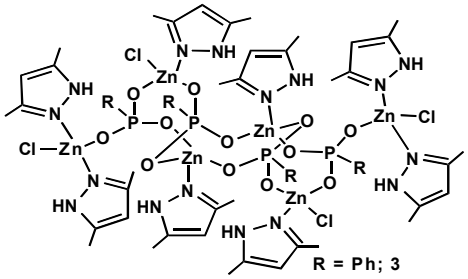

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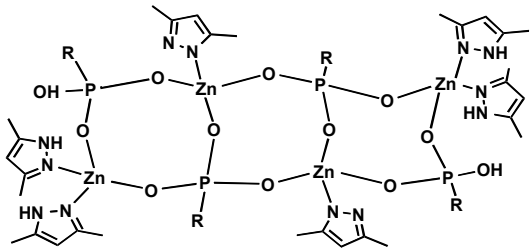
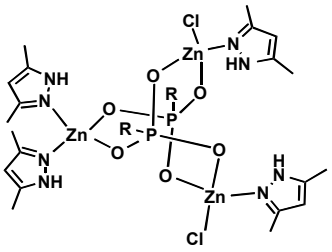


R triisopropylphenyl; Ref. 4



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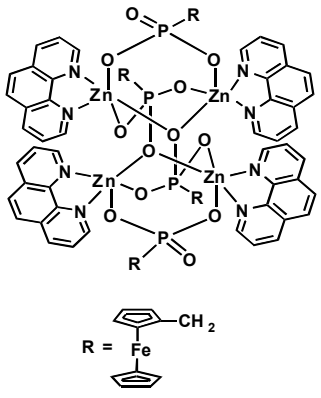

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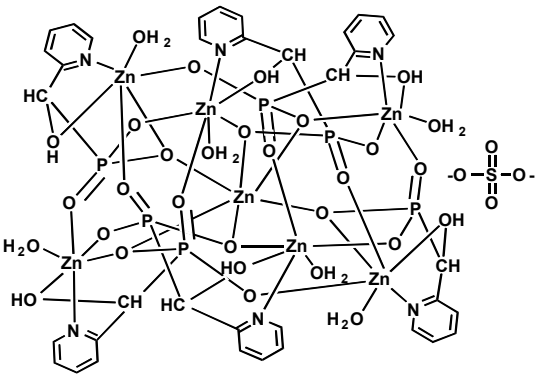

Ref. 6

Chart 1, Structurally Characterized Zinc Phosphonate Clusters.

References: (1)Y. Yang, J.Pinkas, M. Noltemeyer, H.-G. Schmidt, and H. W. Roesky, *Angew. Chem., Int. Ed.* 1999, **38**, 664-666. (2) G. Anantharaman, V. Chandrasekhar, M. G. Walawalkar, H. W. Roesky, D. Vidovic, J. Magull, M. Noltemeyer, *Dalton Trans*. 2004, 1271-1275. (3) V. Chandrasekhar, S. Kingsley, B. Rhatigan, M. K. Lam, and A. L. Rheingold, *Inorg. Chem*. 2002, **41**, 1030-1032. (4)V. Chandrasekhar, P. Sasikumar, R. Boomishankar, and G. Anantharaman, *Inorg. Chem*. 2006, **45**, 3344-3351. (5) J. Wu, Y. Song, E. Zhang, H. Hou, Y. Fan, and Y. Zhu, *Chem.-Euro. J*. 2006, **12**, 5823-5831. (6) D.-K. Cao, Y.-Z. Li and L.-M. Zheng, *Inorg. Chem*. 2005, **44**, 2984-2985.

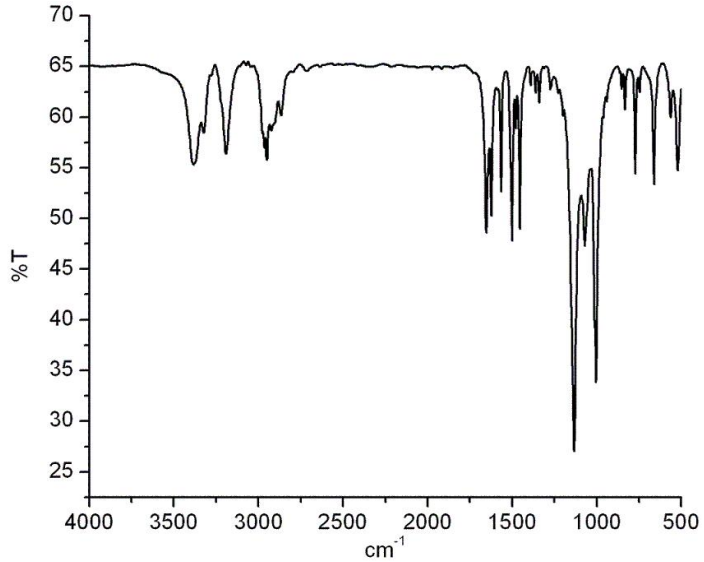

Figure 1. IR spectrum of $[Zn(^{t}BuPO_3)(Py\text{-}2\text{-}NH_2)]_4$ as KBr discs.

The compound $[Zn(^{t}BuPO_3)(Py\text{-}2\text{-}NH_2)]_4$ is insoluble in all solvents. The NMR tube reaction of this compound in CD_3OD shows there is an up-field shift in chemical shift value (δ = 34.79 ppm) which compared to free ligand (δ = 35.5 ppm)

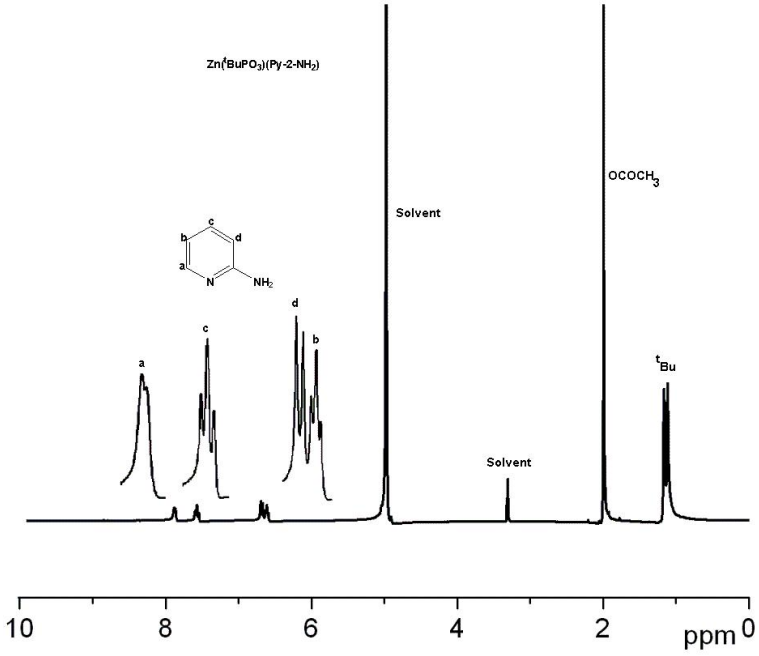

Figure 2. ^{1}H NMR spectrum of $[Zn(^{t}BuPO_3)(Py\text{-}2\text{-}NH_2)]_4$ in CD_3OD.

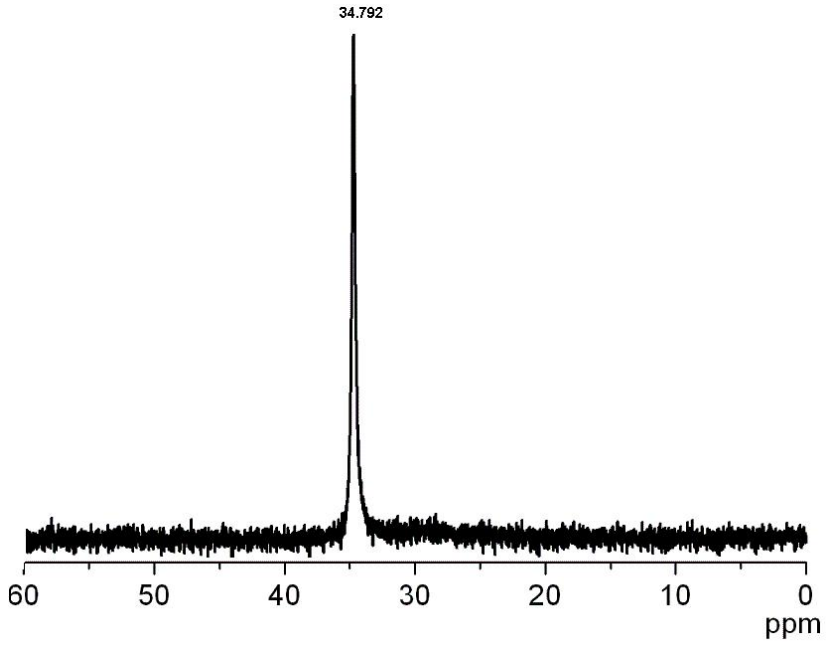

Figure 3. ^{31}P NMR spectrum of $[Zn(^{t}BuPO_3)(Py\text{-}2\text{-}NH_2)]_4$ in CD_3OD.

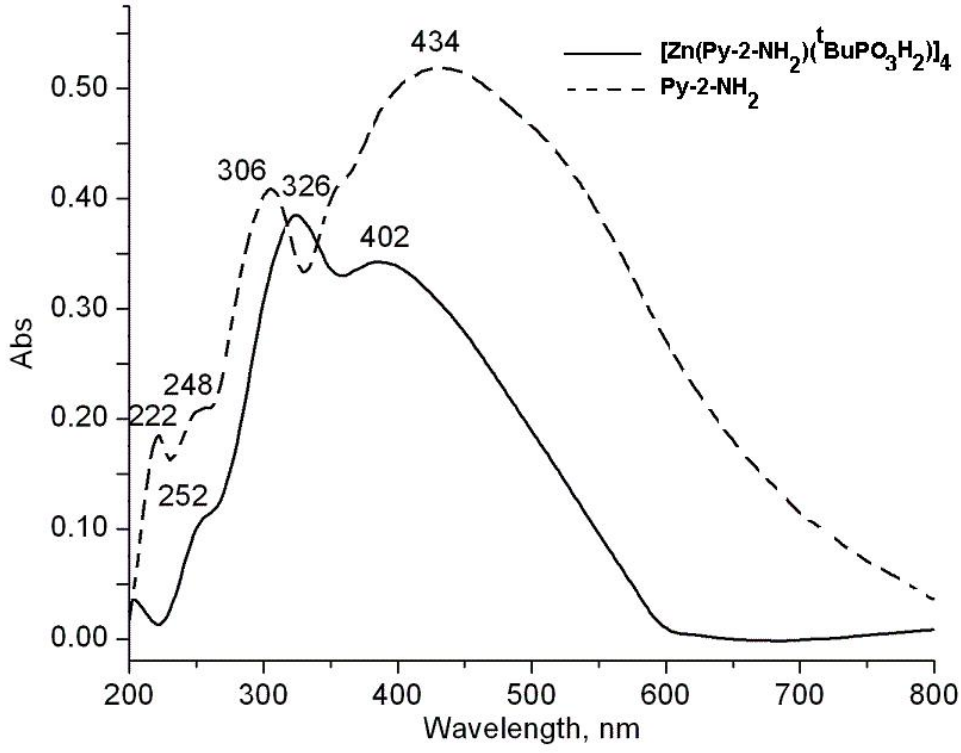

Figure 4. Solid State UV-vis spectra of $[Zn(^{t}BuPO_3)(Py\text{-}2\text{-}NH_2)]_4$ and Py-2-NH_2.

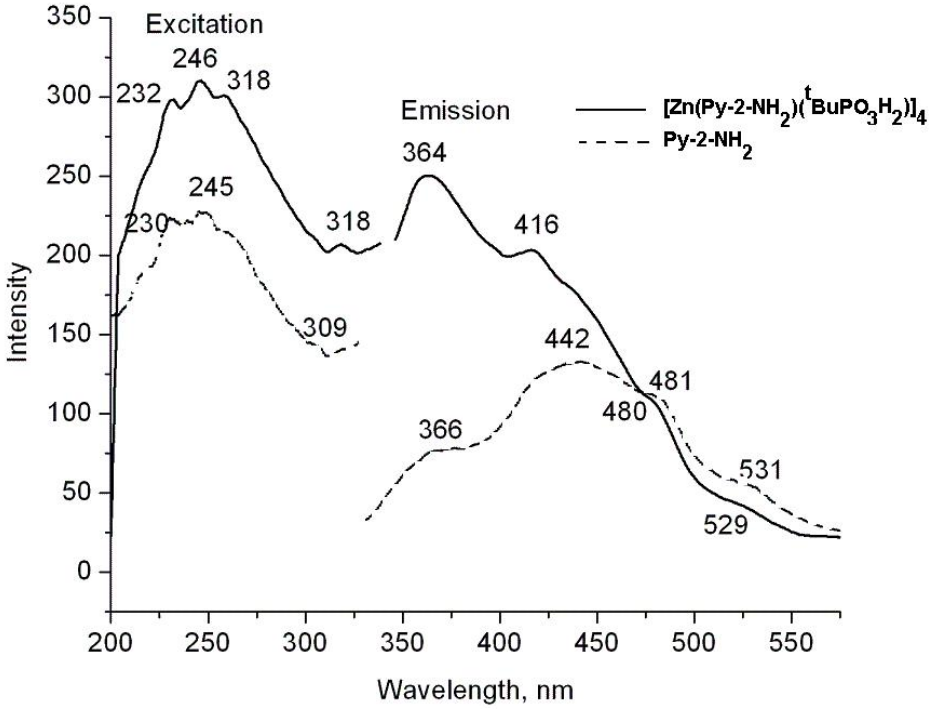

Figure 5. Solid State Fluorescencce spectra of $[Zn(^tBuPO_3)(Py\text{-}2\text{-}NH_2)]_4$ and $Py\text{-}2\text{-}NH_2$.

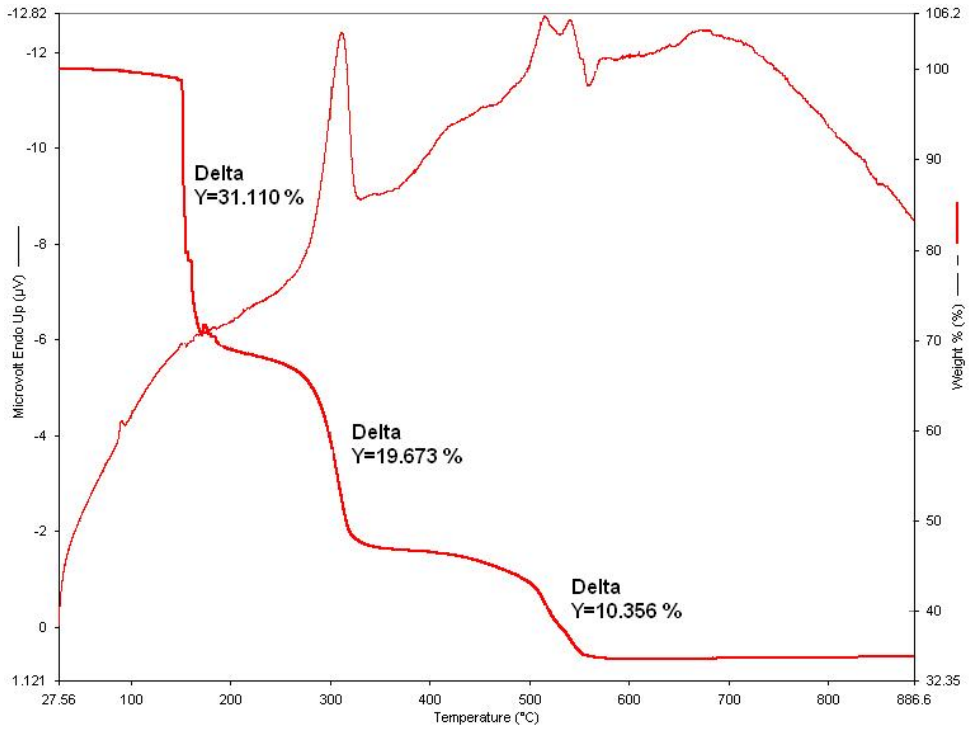

Figure 6. Thermal decomposition of $[Zn(^tBuPO_3)(Py\text{-}2\text{-}NH_2)]_4$.

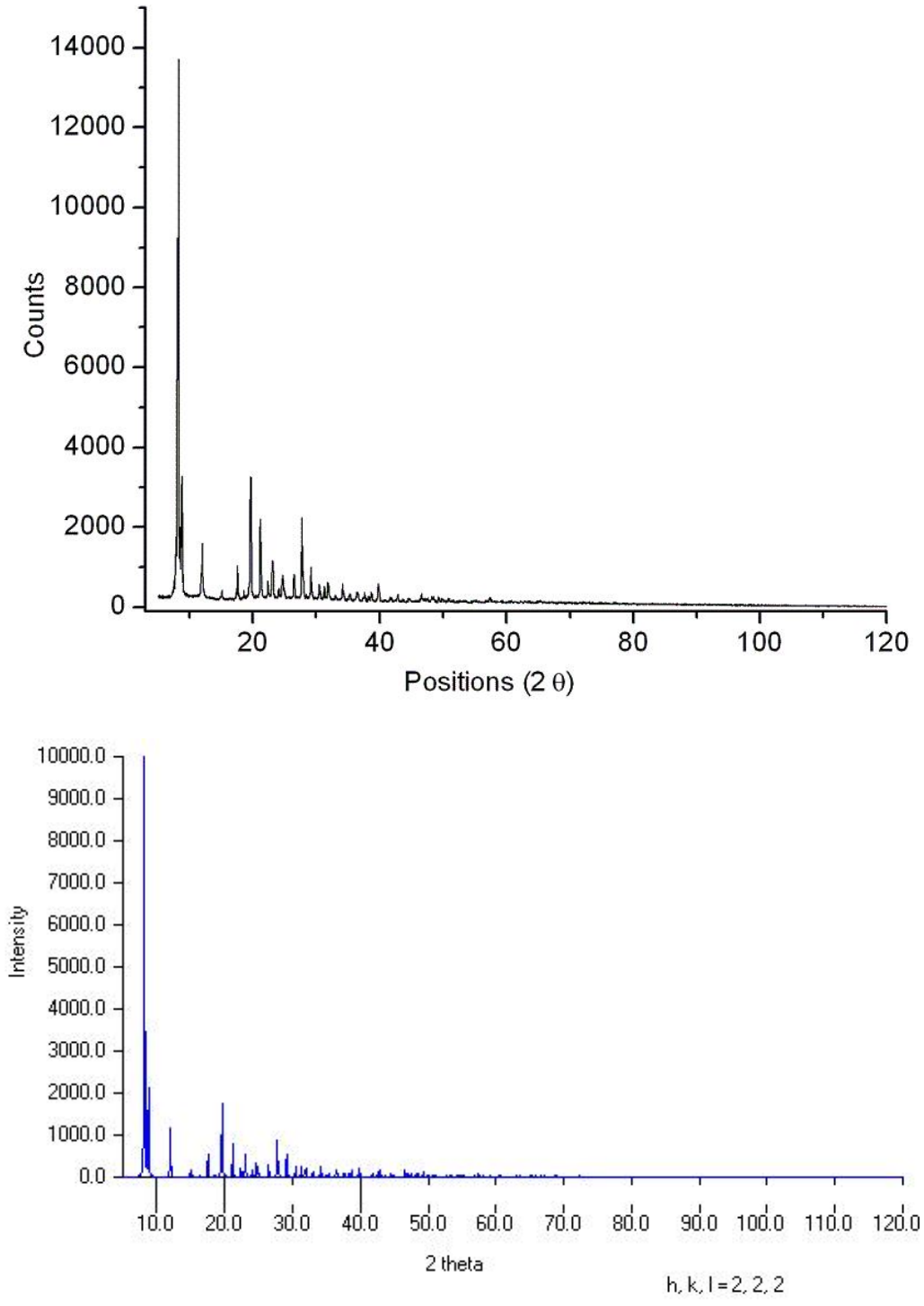

Figure 7. PXRD pattern of $[Zn(^{t}BuPO_3)(Py\text{-}2\text{-}NH_2)]_4$ (top) experimental (bottom) simulated from single crystal data.

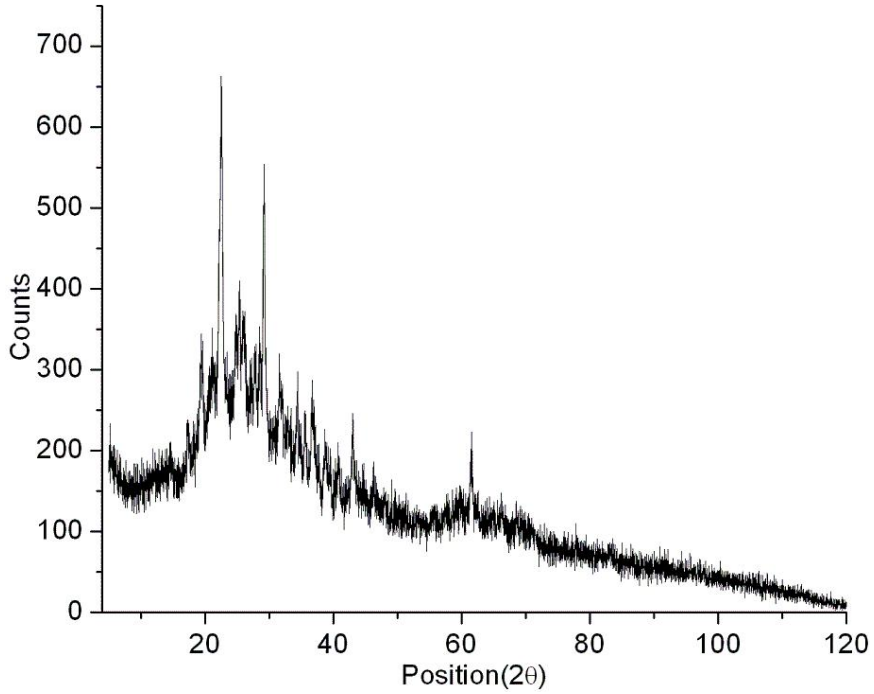

Figure 8. PXRD pattern of $Zn_2P_2O_7$, the thermal drcomposition product derived from $[Zn(^tBuPO_3)(Py\text{-}2\text{-}NH_2)]_4$.

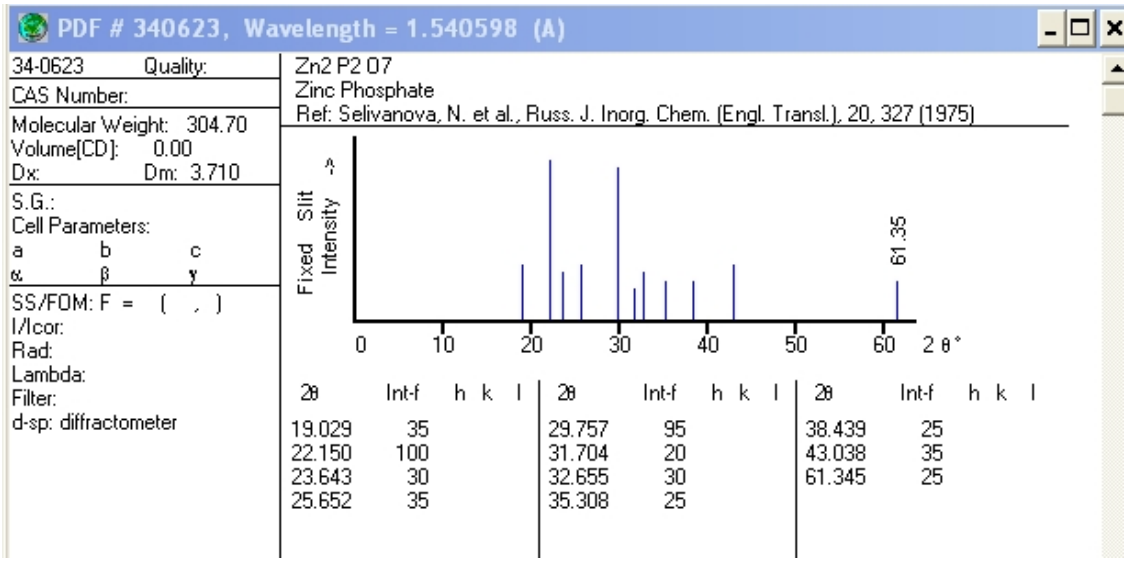

Figure 9. JCPDS file for $Zn_2P_2O_7$ showing good match to the PXRD in Figure 8.

Table 1. Details of hydrogen bonds in 1.

N2-H2A	N2...O3 (1)	H2A...O3 (1)	N2-H2A...O3 (1)
0.860(3)	2.955(4)	2.177(2)	150.3(2)
N2-H2B	N2...O1 (2)	H2B...O1 (2)	N2-H2B...O1 (2)
0.860(3)	2.933(4)	2.135(2)	154.2(2)

Equivalent positions:
(1) y+1/4,-x+3/4,-z+3/4
(2) -x+1,-y,-z+1