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The Crystal and Molecular Structure of Zinc Phenylphosphonate

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A new series of layered divalent transition metal phenylphosphonates has been prepared by reaction between solutions of the metal ions and phenylphosphonic acid. The crystal structure of the zinc compound has been solved, revealing the structure of the layers with pendent phenyl groups in the interlamellar space and unusual coordination behavior of the phosphonate groups.

At the time of writing, we have prepared layered phenylphosphonates of Mg^{2+}, Ni^{2+} and Cu^{2+} which are isomorphous with the zinc compound.

In 1978 Alberti *et al.* [1] reported the synthesis of a zirconium phenylphosphonate, $Zr(O_3PC_6H_5)_2$. This compound has an interlayer spacing of 14.7 Å and fits a model [1, 2] in which the layers maintain the α-zirconium phosphate layer structure [3, 4] with pendent phenyl rings located in the interlamellar space. In order to accommodate the phenyl groups in the available space, it was necessary to tilt the phosphate groups in the model [2] so that the P–O–C bonds were perpendicular to the layers. We have attempted to grow single crystals of the zirconium phenylphosphonate without success. However, a well-defined X-ray powder pattern has been obtained. Solution of the structure from the powder data, in conjunction with the model, is in progress using methods which previously have proven successful [5, 6].

In the meantime, we explored the possibility that divalent first row transition elements would also form layered phenylphosphonates which are more soluble in excess phenylphosphonic acid and therefore more apt to yield single crystals.

Experimental

The zinc compound was obtained as small crystals by adding 0.1 M $ZnCl_2$ slowly to excess 0.1 M phenylphosphonic acid and holding at 60 °C for 10 days. *Anal.* Found: C, 30.64; H, 2.94; H_2O, 7.57.** Calc. for $Zn(O_3PC_6H_5)\cdot H_2O$: C, 30.09; H, 2.95; H_2O, 7.52%.

A clear colorless single crystal (0.05 × 0.1 × 0.2 mm) was mounted and data were obtained on a rotating anode Rigaku AFC-5 computer-automated diffractometer, using Mo Kα radiation. Crystal data: space group, $Pmn2_1$; $a = 5.634(2)$, $b = 14.339(5)$, $c = 4.833(1)$ Å; $Z = 2$. Refinement was carried out using 330 observed reflections for which $I > 3\sigma(I)$ and has progressed to the stage $R_F = 0.055$, $R_{WF} = 0.066$, where the major features of the structure are evident. Two views of the structure are given in Figs. 1A and B and show the layered nature of the compound with pendent phenyl groups. The interlayer distance is given by the *b* axis length.

Results and Discussion

The coordination about the Zn atoms is distorted octahedral, as shown in Fig. 2. Two oxygens (O3) of each phosphonate group chelate a zinc atom and are responsible for the small 64.5° angle in the zinc coordination sphere. At the same time, these chelating oxygens also bridge to adjacent zinc atoms along the *a* axis. They are represented by the O3′ atoms in Fig. 2. The third phosphonate oxygen (O1) bonds to only one zinc atom along the *c* direction. The final coordination site belongs to the water molecule.

The odd shape of the phenyl ring thermal ellipsoids is undoubtedly due to disorder. The rings are 5.63 Å apart in the *a* direction and if they were lying flat, as pictured in Fig. 1B, would experience severe non-bonded hydrogen interactions. It thus appears that they are disordered about the P–C bond. Several disorder models which are based on the observed thermal ellipsoids are under investigation.

The present structure differs considerably from the corresponding zirconium compound. In our model of the latter compound [2] the three phosphonate oxygens are bonded to three different zirconium atoms producing octahedral coordination of Zr with oxygen atoms from six different phosphonate groups. Each oxygen is thus two-coordinate, being bonded to Zr and P. In contrast, zinc phenylphosphonate contains half as many phosphonate groups as the zirconium compound. In order to achieve octahedral coordination, two of the oxygens chelate the zinc and also bridge across zinc atoms and thus are three-coordinate. In addition, a water molecule is required to fill out the metal coordination shell. The chelation-bridging arrangement produces a kinked layer which forces the phenyl rings to approach each other closely, hence the disorder.

The reaction of divalent metals with organic phosphonates appears to be general, as we have

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**As determined by thermogravimetric analysis in the temperature range 80–120 °C.

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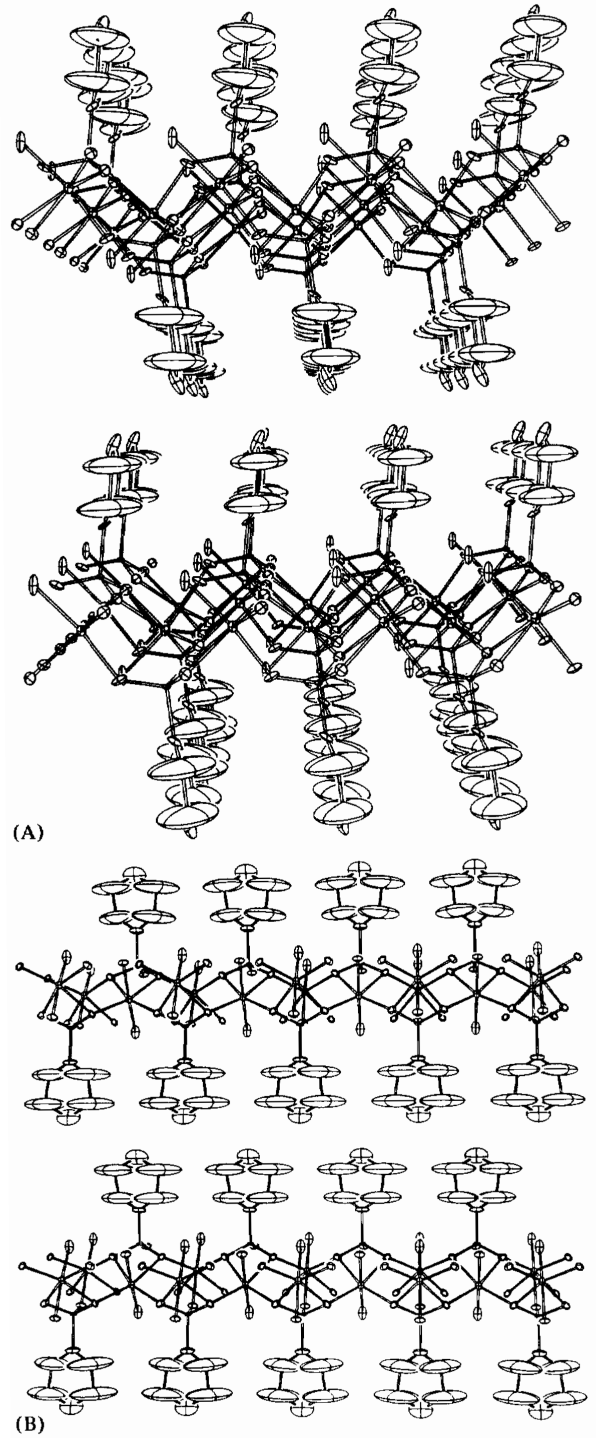

Fig. 1. ORTEP representations of zinc phenylphosphonate looking down the *a* axis (A) and down the *c* axis (B).

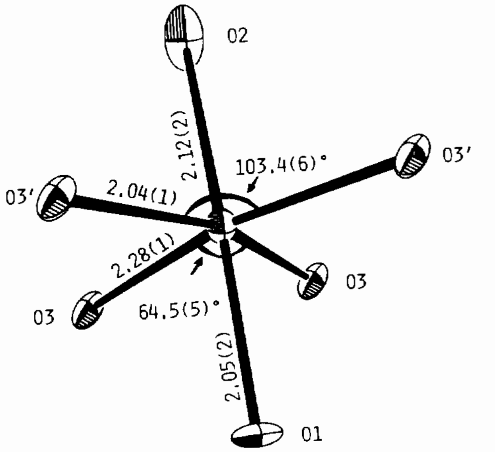

Fig. 2. ORTEP representation of the zinc atom coordination. O2 represents the water molecule and O3 the chelating oxygens. The thermal ellipsoids are at 50% probability level.

prepared a number of other derivatives in which functional groups have been incorporated or are part of the organic moiety. These materials have been characterized by X-ray powder diffraction and thermogravimetric analyses. Based on the similarity of unit cell dimensions and X-ray intensities, the $M(O_3PC_6H_5)\cdot H_2O$ (M = Ni, Cu, Mg) derivatives appear to be isostructural with the Zn phenylphosphonate. This is to be expected, as the $H_2O \rightarrow ZnO_3P$ layers are essentially similar to those found in the series $(NH_4)MO_3PO\cdot H_2O$ where $M = Fe^{2+}$, Cd^{2+}, Mn^{2+} [7–9] and this represents one of the few ways, or perhaps the only way, that a 1:1 ratio of metal and phosphate group can form layers in which the metal is six-coordinate.

Supplementary Material

Tables of atomic parameters, anisotropic thermal parameters, bond distances and angles, and observed *versus* calculated structure amplitudes are available from the authors.

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