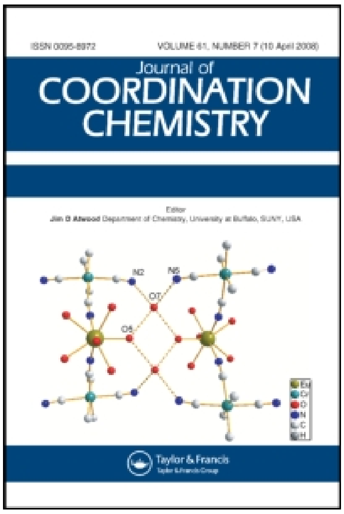

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THE CRYSTAL STRUCTURE OF A ZINC ETHYLENEDIAMINO-*N* METHYL PHOSPHONATE DICHLORIDE

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The title compound, $Zn(O_3PCH_2NH_2CH_2CH_2NH_3)Cl_2$, crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$ and cell parameters $a = 8.348(1)$, $b = 8.269(1)$, $c = 15.220(2)$Å; $\beta = 103.29(1)°$, $V = 1022.5(2)$Å^3. The zinc ion is 4-coordinate being bonded to two chloride ions and two oxygen atoms. Polymeric chains of Zn atoms bridged by the phosphonato group form in a zig zag manner in the crystallographic *b* direction. A strong hydrogen bonding scheme involving both Cl^- ions and the third phosphonato oxygen atoms as acceptors and the protonated amino groups as donors together with the interpenetrant packing of the amine chains causes the structure to be strongly bound in three dimensions.

Keywords: Zinc, phosphonate, chloride, X-ray structure, hydrogen bonding

INTRODUCTION

The group IV cations form an interesting class of layered compounds with organic phosphates and phosphonates.[1-6] These compounds can be prepared with the organic portion containing functional groups[7] or the organic portion can be subsequently functionalized.[8] Recently, vanadyl phosphonates have also been prepared.[9] These compounds have great potential for use as catalysts, ion exchangers and complexing agents. Thus it was of interest to determine whether other groups of cations would form related derivatives. It has now indeed been found that divalent cations also form layered compounds with organic phosphonates.[10,11] The divalent layered phosphonates are related to the inorganic phosphates of the type $NH_4MgPO_4 \cdot H_2O$[11,12] as the four valent organophosphosphonates are to α-$Zr(HPO_4)_2 \cdot H_2O$.[1,13] In a series of forthcoming papers we will explore these relationships. However, during the course of preparing these compounds we isolated a crystalline derivative of ethylenediamino-*N*-methylphosphonic acid. We report here the structure of this compound.

EXPERIMENTAL

Ethylenediamino-*N*-methylphosphonic acid, $NH_2CH_2CH_2NHCH_2PO_3H_2$, was prepared as described in the literature.[14] Zinc chloride (1.36 g, Mallinkrodt reagent grade) was dissolved in 25 cm^3 of water to which was added a solution containing 1.88 g (0.0122 mol) of the phosphonic acid and 3 cm^3 of conc. HCl in 50 cm^3 of

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water. This solution was heated in an oil bath at 60°C for 3 days. A white solid which formed during this time was separated by filtration and the clear filtrate allowed to evaporate slowly at room temperature. After 6 weeks, crystals formed. These were collected and washed with three 10 cm^3 portions of water, then ethanol. The air dried yield was 870 mg. Since the empirical formula was subsequently shown to be $Zn(O_3PCH_2NH_2CH_2CH_2NH_3)Cl_2$, the yield based upon initial zinc content was $\sim$30%.

X-ray Structure Analysis

A colourless crystal of approximate dimensions 0.30 × 0.25 × 0.30 mm was cut from a large tabloid crystal of $Zn(O_3PCH_2NH_2{}^+CH_2CH_2NH_3{}^+)Cl_2$. The crystal fragment was mounted on a glass fibre and crystallographic measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated MoKα radiation ($\lambda K\alpha = 0.71069$Å) using a 12 kW rotating anode generator and CONTROL[15] software. Cell parameters for data collection were obtained from least-squares refinement of 25 carefully centred reflections chosen from the 25–30° 2θ shell immediately preceding data collection; final cell parameters were chosen from the data with 2θ ranging from 49.1 to 50.0°. The unit cell was found to be monoclinic with cell parameters $a = 8.348(1)$, $b = 8.269(1)$, $c = 15.220(2)$Å, $\beta = 103.29(1)°$; $V = 1022.5(2)$Å^3 for $Z = 4$.

Data were collected at 23° ± 1°C using the ω-2θ scan method in shells to a maximum value of 50.0° in 2θ. Standards were chosen automatically based on both intensity and spatial distribution and measured every 150 reflections.

Omega scans of several intense reflections made with a take-off angle of 6.0° prior to data collection, had an average width at half-height of 0.32°. Scans of $(1.63 + 0.30 \tan\theta)°$ were made at a speed of 8.0°/min (in ω). The A value of 1.63°ω was determined experimentally.

The weak reflections ($I < 10.0\sigma(I)$) were rescanned twice and the counts were accumulated to assure good counting statistics. Of the 2074 reflections which were collected, 1934 were unique ($R_{int} = 0.018$); equivalent reflections were merged. The data were corrected for Lorentz and polarization effects. For $Z = 4$ and $M = 288.38$, the calculated density is 1.873 g/cm^3. Based on the systematic absences of $h0l$ ($l \neq 2n$) and $0k0$ ($k \neq 2n$) and the successful solution and refinement of the structure, the space group was determined to be $P2_1/c$.

Structure Solution and Refinement

The structure was solved by direct methods,[16,17] and built up by phase refinement.[18] After full isotropic refinement, an empirical absorption correction, based on azimuthal scans of several reflections, was applied and resulted in transmission factors ranging from 0.92 to 1.00. The linear absorption coefficient for MoKα is 31.1 cm^{-1}. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by difference Fourier methods and refined both positionally and isotropically. The final cycle of full-matrix least-squares refinement[19] was based on 1553 parameters and converged (largest parameter shift was 0.24 times its esd) with unweighted and weighted agreement factors of $R = \Sigma|\,|F_o| - |F_c|\,|\,/\Sigma|F_o| = 0.22$ and $R_w = [(\Sigma w(|F_o| - |F_o|)^2 / \Sigma w F_o{}^2)]^{\frac{1}{2}} = 0.035$.

The standard deviation of an observation of unit weight[20] was 1.15. The weighting scheme was based on counting statistics and included a factor ($p =$ 0.05) to

TABLE I
Positional and thermal parameters for $Zn(O_3PCH_2NH_2CH_2CH_2NH_3)Cl_2$. Estimated standard deviations are given in parentheses.

atom	x/a	y/b	z/c
Zn	0.69540(4)	0.16143(4)	0.25374(2)
Cl1	0.8917(1)	0.1632(1)	0.17278(5)
Cl2	0.7522(1)	−0.0128(1)	0.36956(7)
P	0.60118(8)	0.46545(8)	0.36098(4)
O1	0.4898(2)	0.3537(2)	0.3972(1)
O2	0.6895(2)	0.3839(2)	0.2958(1)
O3	0.4791(2)	0.1225(2)	0.1778(1)
N1	0.7225(3)	0.6822(3)	0.4969(2)
N2	0.7496(4)	0.8570(4)	0.6872(2)
C1	0.7692(3)	0.5346(3)	0.4520(2)
C2	0.8659(3)	0.7591(4)	0.5605(2)
C3	0.8143(4)	0.9043(4)	0.6075(2)
H1	0.802(4)	0.457(4)	0.495(2)
H2	0.860(4)	0.559(4)	0.427(2)
H3	0.680(4)	0.750(4)	0.452(2)
H4	0.647(4)	0.655(4)	0.530(3)
H5	0.902(4)	0.672(4)	0.605(2)
H6	0.941(4)	0.793(4)	0.524(2)
H7	0.724(4)	0.972(4)	0.564(2)
H8	0.915(4)	0.970(4)	0.636(2)
H9	0.845(6)	0.809(5)	0.735(3)
H10	0.723(5)	0.945(5)	0.709(3)
H11	0.666(5)	0.794(5)	0.666(3)

	U11	U22	U33	U12	U13	U23
Zn	0.0218(2)	0.0178(2)	0.0216(2)	−0.0009(1)	0.0040(1)	0.0015(1)
Cl1	0.0328(4)	0.0564(5)	0.0354(5)	0.0019(3)	0.0160(3)	−0.0099(4)
Cl2	0.0559(6)	0.0537(6)	0.0561(6)	−0.0114(4)	−0.0043(4)	0.0350(5)
P	0.0190(3)	0.0177(3)	0.0173(3)	−0.0019(3)	0.0053(3)	−0.0018(3)
O1	0.030(1)	0.031(1)	0.032(1)	−0.0103(8)	0.017(1)	−0.0054(8)
O2	0.032(1)	0.019(1)	−0.026(1)	−0.0054(8)	0.0156(8)	−0.0067(8)
O3	0.028(1)	0.022(1)	0.030(1)	−0.0031(8)	−0.0029(9)	0.0009(8)
N1	0.019(1)	0.021(1)	0.019(1)	−0.0018(9)	0.006(1)	−0.003(1)
N2	0.033(1)	0.038(2)	0.032(2)	−0.006(1)	0.014(1)	−0.014(1)
C1	0.020(1)	0.022(1)	0.021(1)	0.003(1)	0.004(1)	−0.003(1)
C2	0.022(1)	0.028(2)	0.025(2)	−0.007(1)	0.006(1)	−0.006(1)
C3	0.035(2)	0.027(2)	0.033(2)	−0.008(1)	0.010(1)	−0.009(1)
H1	0.032(8)					
H2	0.023(7)					
H3	0.030(9)					
H4	0.05(1)					
H5	0.035(9)					
H6	0.050(10)					
H7	0.023(7)					
H8	0.04(1)					
H9	0.07(1)					
H10	0.06(1)					
H11	0.07(1)					

downweight the intense reflections. Plots of $\Sigma\, w\, (|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.42 and −0.32 e/Å^3, respectively, located around the chlorine atoms.

Neutral atom scattering factors were taken from Cromer and Waber.[21] Anomalous dispersion effects were included in F_c;[22] the values for Δf′ and Δf″ were those of Cromer.[23]

Final positional and anisotropic thermal parameters are given in Table I, important bond distances and angles in Table II. A structure factor listing (Table SI) is

TABLE II
Bond distances (Å) and Angles (deg.) with estimated standard deviations in parentheses.

atom 1	atom 2	distance	atom 1	atom 2	distance
Zn	O3	1.934(2)	N2	H10	0.85(4)
Zn	O2	1.952(2)	N2	H11	0.87(4)
Zn	Cl2	2.2414(9)	N2	H9	1.02(4)
Zn	Cl1	2.2652(8)	N2	C3	1.489(4)
P	O1	1.503(2)	C1	H1	0.91(3)
P	O3	1.517(2)	C1	H2	0.94(3)
P	O2	1.523(2)	C2	H6	0.97(4)
P	C1	1.822(3)	C2	H5	0.98(3)
N1	H3	0.89(3)	C2	C3	1.510(4)
N1	H4	0.92(4)	C3	H8	1.01(3)
N1	C1	1.494(3)	C3	H7	1.05(3)
N1	C2	1.497(3)			

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
O3	Zn	O2	105.21(8)	H10	N2	C3	106(3)
O3	Zn	CL2	111.26(6)	H11	N2	H9	117(4)
O3	Zn	CL1	111.63(7)	H11	N2	C3	105(3)
O2	Zn	CL2	111.40(6)	H9	N2	C3	108(3)
O2	Zn	CL1	104.36(6)	H1	C1	H2	108(2)
Cl2	Zn	CL1	112.54(4)	H1	C1	N1	108(2)
O1	P	O3	114.4(1)	H1	C1	P	112(2)
O1	P	O2	113.6(1)	H2	C1	N1	109(2)
O1	P	C1	110.3(1)	H2	C1	P	108(2)
O3	P	O2	111.2(1)	N1	C1	P	111.6(2)
O3	P	C1	102.8(1)	H6	C2	H5	118(3)
O2	P	C1	103.4(1)	H6	C2	N1	106(2)
P	O2	Zn	133.1(1)	H6	C2	C3	110(2)
P	O3	Zn	130.0(1)	H5	C2	N1	102(2)
H3	N1	H4	111(3)	H5	C2	C3	110(2)
H3	N1	C1	105(2)	N1	C2	C3	111.8(2)
H3	N1	C2	110(2)	H8	C3	H7	113(3)
H4	N1	C1	109(2)	H8	C3	N2	102(2)
H4	N1	C2	108(2)	H8	C3	C2	110(2)
C1	N1	C2	112.9(2)	H7	C3	N2	108(2)
H10	N2	H11	113(4)	H7	C3	C2	111(2)
H10	N2	H9	107(3)	N2	C3	C2	111.9(3)

available as supplementary material from the authors (11 pages). The molecular unit together with the atom numbering scheme is given in Figure 1, and the polymeric structure of the material shown in Figure 2.

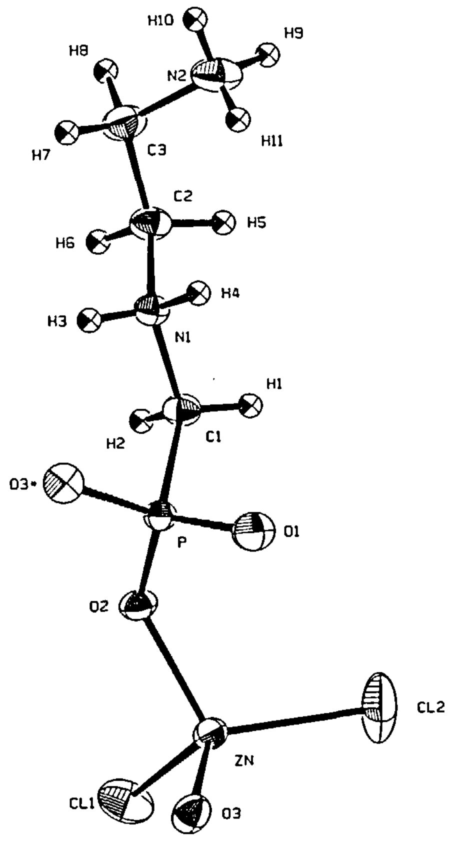

FIGURE 1 Molecular unit in the title compound showing the tetrahedral Zn atom, the ligand conformation and atom numbering scheme. 03* is a symmetry equivalent of 03. Non-hydrogen thermal ellipsoids represent 50% probability.

RESULTS AND DISCUSSION

The zinc atom is tetrahedrally coordinated by two chlorine and two phosphonato oxygen atoms as shown in Figure 1. The phosphonato oxygens come from two different NNP* ligands causing the Zn atoms to be linked by phosphonate bridges. The bridging forms zig zag chains along the *b* direction and the phosphonate groups are alternately above and below the mean lines of Zn atoms which are at *ca* $z = 0.25$ and 0.75. The uncoordinated end of the NNP ligand is therefore alternately above and below the lines of zinc atoms as shown in Figure 2. The overall effect is a herringbone packing of the NNP ligands.

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* NNP = $[NH_3CH_2CH_2NH_2CH_2PO_3]$

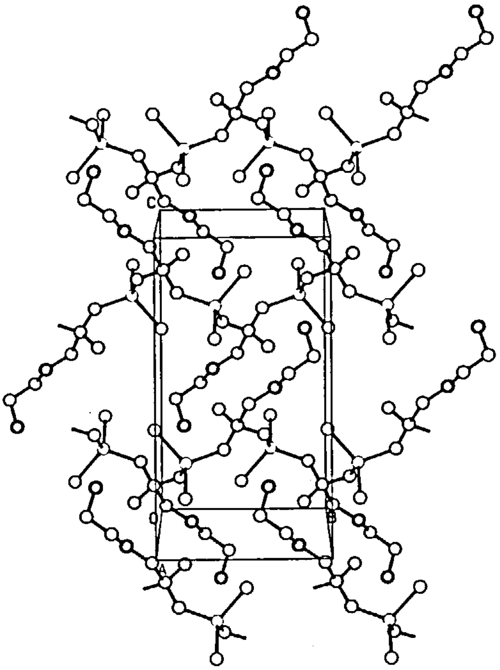

FIGURE 2 Cell contents showing the polymeric arrangement along the *b* direction. Hydrogen atoms are omitted for clarity. Thickly lined circles are nitrogen atoms.

The phosphonate group is nearly perfectly tetrahedral and has P–O, P–C distances typical of such ligand types.[24,25] Bond distances and angles in the zinc tetrahedra are also regular. Each of the nitrogen atoms in the NNP chain is protonated. The phosphonate group is somewhat changed from the phosphonomethylglycine extended complex. This is seen by the torsional angles of O_{coord}-P–N–C = 57.1°[24] *versus* O3-P–Cl–N1 = 81.5° (Table III). The overall charge on the phosphonato group is 2– and the chlorides also contribute an equal negative charge. This means that for charge balance in the structure (Figure 1) both nitrogen centres are required to be protonated. This is reasonable considering the high acidity at which the crystals were prepared, but yields a ligand with three separate charge centres. While this is unusual in this type of complexed material, carbonato functionalities have been seen to be protonated in other phosphonato ligands.[25] The charge separation, together with the three dimensional packing of the structure, is stabilized by a series of strong hydrogen bonds Cl1 is hydrogen bonded to N2 *via* H9 (Cl1–N2 3.256(3), Cl1–H9 2.34(5)Å) in the *ac* direction. Cl2 hydrogen bonds to N1 (3.225(3)Å *via* H3 (2.48(3)Å) in the *bc* direction. Hydrogen bonding also occurs with the free phosphonate oxygen O1 to N1 (2.672(3)Å) *via* H4 (1.77(4)Å) in the *ac* direction and also to N2 (2.739(3)Å) *via* H11 (1.88(5)Å) in the *ab* direction. N2 also forms hydrogen bonds to coordinated 02 (2.820(3)Å) with H10 (2.00(4)Å) in the *bc* direction as does O3 to N1 (2.844(3)Å *via* H3 (2.36(3)Å) in the *ac* direction. This hydrogen bonding scheme apparently determines the conformation of the NNP ligand and in turn the herringbone packing of the NNP ligands.

TABLE III
Torsion or conformation angles[a] with estimated standard deviations in parentheses.

Atom					Atom				
(1)	(2)	(3)	(4)	angle(°)	(1)	(2)	(3)	(4)	angle(°)
Zn	O3	P	O1	90.6(2)	Cl2	Zn	O2	P	−50.7(2)
Zn	O3	P	O2	29.4(4)	P	O3	Zn	O2	−74.1(2)
Zn	O3	P	C1	60.2(2)	P	O2	Zn	O3	70.0(2)
Zn	O2	P	O1	−3.3(2)	P	C1	N1	C2	−169.8(2)
Zn	O2	P	O3	−134.1(2)	O1	P	C1	N1	−87.2(2)
Zn	O2	P	C1	116.2(2)	O2	P	C1	N1	151.0(2)
Cl1	Zn	O3	P	79.2(2)	O3	P	C1	N1	81.0(3)
Cl1	Zn	O2	P	−172.4(1)	N1	C2	C3	N2	82.7(3)
Cl2	Zn	O3	P	−47.4(2)	C1	N1	C2	C3	−177.9(2)

[a] The sign is positive if, when looking from atom 2 to atom 3, a clockwise motion of atom 1 would superimpose it on atom 4.

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20. Standard deviation of an observation of unit weight: $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o = number of observations and N_v = number of variables.
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