

The Crystal Structure of Trisodium Cadmium Triphosphate

$\text{Na}_3\text{CdP}_3\text{O}_{10} \cdot 12\text{H}_2\text{O}$ *

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Within investigations of the bonding of different metal ions to the triphosphate ion $\text{P}_3\text{O}_{10}^{5-}$, the crystal structure of the compound $\text{Na}_3\text{CdP}_3\text{O}_{10} \cdot 12\text{H}_2\text{O}$ has now been determined. It represents the first example of a tridentate bonding of the $\text{P}_3\text{O}_{10}^{5-}$ group to a divalent metal. Trisodium cadmium triphosphate belongs to a series of isomorphous compounds $\text{Na}_3\text{M(II)P}_3\text{O}_{10} \cdot 12\text{H}_2\text{O}$ with $\text{M(II)} = \text{Mg, Mn, Co, Ni, Zn}$ and Cd ,¹ the structures of which have not been previously determined.

$\text{Na}_3\text{CdP}_3\text{O}_{10} \cdot 12\text{H}_2\text{O}$ was first prepared by Glühmann² and its existence was confirmed by Bonneman-Bemia³ in a study of the system $\text{Na}_5\text{P}_3\text{O}_{10} - \text{CdCl}_2 - \text{H}_2\text{O}$. It can also be prepared by precipitation from the system $\text{Na}_5\text{P}_3\text{O}_{10} - \text{CdSO}_4 - \text{H}_2\text{O}$.⁴ Stability constants for the formation of the 1:1 complex in aqueous solution have been reported^{5,6} and solubilities for the cadmium salts have been determined.^{7,8}

Single crystals of $\text{Na}_3\text{CdP}_3\text{O}_{10} \cdot 12\text{H}_2\text{O}$ were grown by slow evaporation from a solution, about 0.2 M in $\text{Na}_5\text{P}_3\text{O}_{10}$ and in CdSO_4 , at 5 °C over silica gel in a desiccator. The solution of $\text{Na}_5\text{P}_3\text{O}_{10}$ was prepared from sodium triphosphate hexahydrate obtained by dissolving the anhydrous salt (Kebo, pure) in water and recrystallizing five times according to Qvimby.⁹ The crystals of $\text{Na}_3\text{CdP}_3\text{O}_{10} \cdot 12\text{H}_2\text{O}$ were identified by paper chromatography and by X-ray powder photographs.^{1,10}

Weissenberg and precession photographs showed the crystals to have Laue symmetry $2/m$ and the space group $P2_1/n$.¹¹ A crystal with the approximate dimensions $0.25 \times 0.20 \times 0.18$ mm was used for intensity measurements with a Syntex $P2_1$ automatic four-circle diffractometer

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Table 1. Final positional parameters for $\text{Na}_3\text{CdP}_3\text{O}_{10} \cdot 12\text{H}_2\text{O}$. All atoms occupy position 4(e) in space group nr. 14: $P2_1/n$ [equiv. positions; $\pm(x, y, z)$; $\pm(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$].

Atom	x	y	z
Cd	0.24777(3)	0.04015(4)	0.31438(3)
P1	0.78859(10)	0.34541(16)	0.01724(9)
P2	0.40667(10)	0.26906(16)	0.40513(10)
P3	0.10655(10)	0.27635(16)	0.41165(10)
Na1	0.6447(2)	0.4638(3)	0.2096(2)
Na2	0.8863(2)	0.3052(4)	0.1995(2)
Na3	0.2536(2)	0.2616(3)	0.0616(2)
O1	0.2484(3)	0.0176(5)	0.4669(3)
O2 ^a	0.2502(4)	0.0471(5)	0.1653(3)
O3 ^a	0.1539(3)	0.3505(5)	0.1759(3)
O4	0.3577(3)	0.2014(5)	0.3286(3)
O5 ^a	0.3565(3)	0.3534(5)	0.1764(3)
O6	0.1361(3)	0.1991(5)	0.3282(3)
O7 ^a	0.3715(4)	0.1500(6)	0.9822(3)
O8	0.3529(3)	0.2271(5)	0.4953(3)
O9	0.1904(3)	0.2719(5)	0.4800(3)
O10	0.4994(3)	0.2077(5)	0.4222(3)
O11	0.4054(3)	0.4296(5)	0.3998(3)
O12	0.0280(3)	0.2050(5)	0.4542(3)
O13	0.0959(3)	0.4347(4)	0.3950(3)
O14 ^a	0.6188(4)	0.2366(7)	0.2779(3)
O15 ^a	0.7747(4)	0.0285(6)	0.1570(4)
O16 ^a	0.8041(4)	0.2036(6)	0.3229(3)
O17 ^a	0.5198(3)	0.4405(5)	0.1099(3)
O18	0.7535(3)	0.3483(5)	0.1152(3)
O19 ^a	-0.0069(3)	0.4171(5)	0.1045(3)
O20 ^a	0.9847(3)	0.1037(6)	0.2132(4)
O21 ^a	0.9325(6)	0.4828(7)	0.3096(6)
O22 ^a	0.1435(3)	0.1308(5)	0.9809(3)
H1	0.288(6)	0.521(11)	0.348(8)
H2	0.251(7)	0.544(11)	0.378(7)
H3	0.140(6)	0.316(10)	0.215(6)
H4	0.088(6)	0.413(9)	0.160(6)
H5	0.412(6)	0.368(10)	0.163(6)
H6	0.376(6)	0.308(10)	0.216(6)
H7	0.395(6)	0.075(11)	0.011(6)
H8	0.388(6)	0.214(10)	0.967(6)
H9	0.100(6)	0.346(10)	0.747(6)
H10	0.107(7)	0.269(11)	0.815(6)
H11	0.246(6)	0.475(9)	0.581(6)
H12	0.257(6)	0.403(11)	0.637(6)
H13	0.230(6)	0.307(10)	0.823(5)
H14	0.305(6)	0.234(10)	0.854(6)
H15	0.430(6)	0.524(8)	0.830(6)
H16	0.031(6)	0.119(10)	0.573(6)
H17	0.488(5)	0.099(9)	0.533(6)
H18	0.490(6)	-0.014(11)	0.382(7)
H19	-0.005(6)	0.052(9)	0.166(7)
H20	0.022(6)	0.110(10)	0.272(6)
H21	0.010(6)	0.431(9)	0.326(6)
H22	0.410(12)	-0.025(19)	0.802(14)
H23	0.092(6)	0.183(9)	0.963(6)
H24	0.140(6)	0.067(9)	0.028(6)

^a H_2O .

employing MoK α -radiation ($\lambda=0.7107 \text{ \AA}$). For a region in 2θ up to 50° 3690 independent reflections were obtained, 3248 of which had intensities larger than $1.96 \sigma(I)$. The ω -scan technique was used with scan speeds from $0.5^\circ \text{ min}^{-1}$ up to $29.5^\circ \text{ min}^{-1}$. Four check reflections were measured regularly at intervals of 50 reflections and they showed no systematic variations during the data collection.

A semiempirical absorption correction was applied. The angular coordinates of 15 accurately centered reflections were used for a least squares refinement of the unit cell constants: $a=14.835(12)$, $b=9.397(10)$, $c=15.244(9) \text{ \AA}$, $\beta=90.20(6)^\circ$, $V=2125.1 \text{ \AA}^3$.

All calculations were carried out with the use of the Syntex XTL crystallographic program system.

The positions of the four cadmium atoms in the unit cell were derived from the three-dimensional Patterson function. All other non-hydrogen atoms could be located from subsequent difference maps. A full matrix least squares refinement of the non-hydrogen atoms in which $\sum w||F_o|-|F_c||^2$ was minimized with the weighting function $w^{-1}=\sigma^2|F_o|+(0.05 F_o)^2$, led to $R=0.050$ and $R_w=0.087$, with anisotropic temperature coefficients and with anomalous dispersion corrections included. From a difference map calculated at this stage of the refinement all 24 hydrogen atoms in the unit cell could be located. After including the 24 H positions in the least squares refinement with isotropic temperature coefficients ($\beta=4.0 \text{ \AA}$) the R values were lowered to $R=0.047$ and $R_w=0.081$. Including unobserved reflections the values were 0.055 and 0.086 respectively. In the final cycle shifts were below about 10 % of the corresponding standard deviations except for some of the hydrogen atoms.

Final positional parameters are given in Table 1. Selected bond lengths are listed in Table 2. Observed and calculated structure factors and temperature factors are available on request from the authors (G. J.).

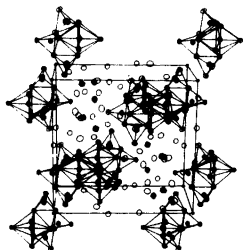


Fig. 1. The unit cell viewed along the b axis with the c axis horizontal.

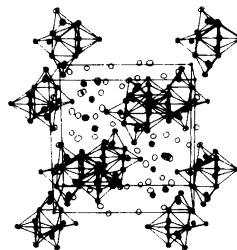
Table 2. Selected bond lengths (\AA) and angles ($^\circ$).

Within the triphosphate group			
P1-O1	1.506(5)		
-O8	1.593(5)		
-O9	1.599(5)	P1-P2	2.988(2)
-O18	1.495(4)	-P3	2.994(2)
P2-O4	1.513(4)	P2-P1-P3	96.25(6)
-O8	1.640(5)	P1-O8-P2	135.2(3)
-O10	1.513(4)	P1-O9-P3	136.8(3)
-O11	1.510(5)		
P3-O6	1.530(4)		
-O9	1.620(5)		
-O12	1.495(5)		
-O13	1.518(4)		
Around cadmium			
Cd-O1	2.335(4)	Cd-P1	3.278(1)
-O2 ^a	2.274(7)	-P2	3.475(2)
-O3 ^a	2.307(5)	-P3	3.396(2)
-O4	2.236(4)		
-O5 ^a	2.344(5)		
-O6	2.241(4)		

^a H₂O.

A steric view of the contents of the unit cell is given in Fig. 1.¹² The triphosphate group is bonded to the cadmium ion by three oxygen atoms, one from each PO₄ tetrahedron. This tridentate bonding is illustrated in Fig. 2. The octahedral coordination around Cd²⁺ is completed by three water molecules and the structure can be described as being built up from CdP₃O₁₀(H₂O)₃²⁻ groups held together by Na⁺ ions and hydrogen bonds.

The Cd-O bonds within the CdO₆ octahedron show significant differences. The two bonds Cd-O₄: 2.236(4) \AA and Cd-O₆: 2.241(4) \AA , which involve oxygens belonging to the terminal phosphate groups, are significantly shorter than the Cd-O bond of 2.335(4) \AA to the central PO₄ tetrahedron. The average length of the bonds to



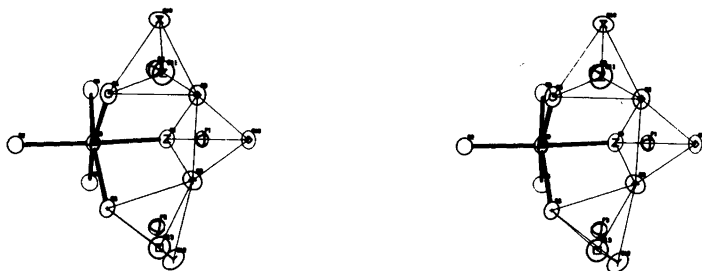


Fig. 2. A steric view of the triphosphate group and the coordination around cadmium.

the water oxygens, O_2 , O_3 and O_5 , is 2.308 Å which is larger than the average bond length to the phosphate oxygens, 2.271 Å (Table 2).

Bond lengths within the P_3O_{10} group are similar to those found in other structures. The P–O bonds to the bridging oxygens are significantly longer (av. value 1.613 Å) than those to the non-bridging oxygens (av. value 1.510 Å). The P–O–P angles ($P_1-O_8-P_2=135.2^\circ$ and $P_1-O_9-P_3=136.8^\circ$) are, however, somewhat larger than for known structures of other two valent metal triphosphates^{13,14} where the corresponding angles have been found to be close to 130° .

No hydrogen atoms are bonded to oxygens of the P_3O_{10} group but the non-bridging oxygens of the two terminal PO_4 tetrahedra are each involved in between two and four hydrogen bonds to surrounding water molecules. The two non-bridging oxygens of the central PO_4 tetrahedron are not involved in H-bonding but are in close contact with sodium ions.

The sodium ions are irregularly coordinated to five (Na_2) or six ($Na_{1,3}$) oxygens, most of them water molecules. The aquated sodium ions occupy the canals between the triphosphate groups.

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