C) intersects the plane defined by the atoms B, N_2, and N_4 (plane D) to form an angle of 109.6°. The Pt–B nonbonded distance, 3.32 (2) Å, is consistent with the value found in a similar complex containing a carbonyl ligand.[4,5]

The angle formed by the intersection of the two complexed pyrazolyl rings, planes E and F, is 131.4°. The plane of the uncomplexed ring (plane G) intersects planes E and F to form angles of 119.1 and 109.4°, respectively. The boron atom and the platinum atom are respectively 0.13 and 0.11 Å out of plane E, 0.11 and 0.11 Å out of plane F, and 0.07 and 0.32 Å out of plane G.

The bonding about the boron atom is tetrahedral. The distance B–N(6) is 0.06 Å shorter than the average of the two other B–N bond lengths. Applying the Cruickshank criteria[15] this difference ($\Delta l/\sigma l = 2.30$) is possibly significant.

The Pt–C(methyl) distance in this compound is 2.12 Å, whereas the corresponding values in the other two cleavage products from $(CH_3)[HB(C_3N_2H_3)_3]Pt$ whose structures have been reported[4,5,10] are 2.07 Å in each case. The average Pt–C(methyl) distances in several compounds is 2.06 ± 0.06 Å (cf. ref 5 and references contained therein). Thus the value observed in this work falls within an acceptable range.

The Pt–C(isocyano) distance is normal and the terminally bonded *tert*-butylisocyano ligand possesses the expected geometry. The average C–C–C angle centering on atom C(3) is 112 (5)° and reflects the large thermal motions associated with the three methyl groups.

The two independent Pt–N distances in this structure are highly significantly different based upon the Cruickshank criteria,[15] $\Delta l/\sigma l = 7.15$. The sense of this difference is consistent with the σ-bonded methyl group's exerting a stronger *trans* influence than the isocyano ligand, as predicted by Appleton, Clark, and Manzer.[16]

The observed "bite" angle of the bidentate chelating ligand in this work is 89.0 (3)° and is consistent with the value (87.4 (3)°) observed in a related four-coordinate complex.[4,5]

The shortest intermolecular contact distance involving the platinum atom and any atom of the uncoordinated pyrazolyl ring is Pt···CN(2) (4.58 Å). The shortest intermolecular contact distance involving two nonhydrogen atoms is 3.35 Å (C9···C9). Thus no intermolecular contact distances are significantly shorter than the sum of their respective van der Waals radii.

In conclusion, an attempt to correlate the solid-state structure and the solution NMR spectra of this compound is appropriate. The NMR spectra of $Pt(CH_3)[HB(pz)_3]$-(CN-*t*-Bu) have been recorded over a wide temperature range[6] and indicate stereochemical nonrigidity. The high-temperature limiting spectra showed the presence of three equivalent pyrazolyl rings, each showing coupling to ^{195}Pt. At low temperatures the spectra showed the presence of two sets of pyrazolyl rings in the ratio of 2:1, each showing ^{195}Pt satellites and confirming the five-coordinate stereochemistry. Detailed NMR line shape analyses of the variable-temperature spectra of the CN-*t*-Bu and other complexes were consistent only with five-coordinate trigonal-bipyramidal structures in solution. The differences in structure in the solution and in the solid state must reflect the similarities in energy between the four- and five-coordinate species.

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Registry No. $(CH_3)[HB(pz)_3]Pt[CNC(CH_3)_3]$, 60104-27-0.

Supplementary Material Available: Listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Crystal Structure of Cobalt(II) Orthophosphate Monohydrate, $Co_3(PO_4)_2 \cdot H_2O$

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A new monohydrate of cobalt(II) orthophosphate has been prepared and its crystal structure determined and refined by full-matrix least-squares procedures using automatic diffractometer data to a residual $R = 0.048$ ($R_w = 0.065$) with a data/parameter ratio of 13. The space group is $P2_1/c$ with $a = 9.516$ (6), $b = 7.904$ (4), $c = 9.277$ (6) Å, and $\beta = 114.22$ (4)°. Divalent cobalt ions occupy three distinct coordination polyhedra: Co(1) and Co(2) are surrounded by six oxygens while Co(3) is five-coordinated. The water oxygen bridges an edge shared by a pair of Co(2) polyhedra across a center of symmetry. Details of the structure are presented as well as the probable location of hydrogen bonds.

Introduction

We have found that single crystals of hydroxyphosphates of the type $M_5(PO_4)_2(OH)_4$,[1] $M_5(PO_4)_3(OH)$,[2] and M_2-$(PO_4)(OH)$[1] can be grown hydrothermally from solutions containing a slight excess of phosphoric acid. During the investigation of the preparation of a hydroxyphosphate of the type $Co_2(PO_4)(OH)$ by hydrothermal reaction of $Co_3(PO_4)_2$ in phosphoric acid solutions, we observed the formation of a new phase which proved to be a monohydrate of cobalt orthophosphate.

Very little has been reported on the hydrates of cobalt(II)

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Table I. X-Ray Powder Diffraction Pattern of $Co_3(PO_4)_2 \cdot H_2O^a$

$a = 9.523$ (3) Å
$b = 7.903$ (2) Å
$c = 9.294$ (3) Å
$\beta = 114°$ 15 (1)′

hkl	*I*	d_{obsd}	d_{calcd}	*hkl*	*I*	d_{obsd}	d_{calcd}
−110	20	5.816	5.844	−411	10	2.247	2.250
−111	5	5.569	5.587	230			2.252
−102	6	4.621	4.630	−304	13	2.191	2.192
002	8	4.233	4.237	222	8	2.144	2.144
−211	7	4.055	4.060	−314	10	2.112	2.112
020	18	3.948	3.952	132	15	2.064	2.061
210	45	3.795	3.805	123	19	2.059	2.058
012	10	3.728	3.734	040	24	1.9762	1.9758
021	16	3.576	3.581	312	28	1.9689	1.9682
−121	10	3.532	3.534	140	8	1.9274	1.9265
211	17	3.079	3.081	−414	13	1.9167	1.9160
−302	27	3.034	3.042	411	11	1.8671	1.8670
−311	8	2.934	2.938	042	16	1.7921	1.7906
022	72	2.887	2.890	−234	10	1.7390	1.7391
−312	8	2.836	2.839	−521	14	1.6825	1.6812
−213	100	2.794	2.802	−341	17	1.6780	1 6760
310	10	2.716	2.718	332	7	1.6101	1.6091
202	12	2.552	2.553	−602	17	1.5833	1.5826
130	41	2.520	2.521	515	11	1.5496	1.5493
212	21	2.428	2.429	−235	14	1.5185	1.5185
311	8	2.336	2.339	−406	13	1.4988	1.4981
−231	23	2.297	2.302	−106	19	1.4944	1.4946
023			2.298	521	10	1.4667	1.4657
−412	10	2.265	2.267	−534	7	1.4521	1.4506

^{a} Powder diffractometer data; Cu $K\alpha_1$ radiation.

phosphate. Mellor[3] reports the existence of a di-, tetra-, and octahydrate. Ando et al.[4] report the stepwise loss of water on heating the octahydrate; 6 H_2O are lost at 150 °C, an additional 1.5 H_2O at 160 °C, and the remaining water at 600 °C.

As there has been no definitive report on the existence of a monohydrate we have completed a detailed x-ray structural analysis; this paper describes the results of our structure determination.

Experimental Section

Preparation. Reaction of $Co_3(PO_4)_2$ in an aqueous 0.1 M H_3PO_4 solution sealed in a welded gold capsule at 400 °C and 55 000 psi resulted in the formation of dark violet euhedral crystals up to 0.15 mm on edge which proved to be $Co_3(PO_4)_2 \cdot H_2O$.

X-Ray Diffraction Data. A powder diffraction pattern was taken of a sample of ground single crystals on a Norelco diffractometer equipped with a graphite monochromator at a scan speed of $^1/_4$° 2θ/min using Cu $K\alpha$ radiation. KCl was used as an internal standard. Table I presents the result of a least-squares refinement of these data indexed on the basis of a monoclinic cell. The assignment of Miller indices was made with the aid of the single crystal intensity data; the reported intensities represent peak heights.

A crystal was ground to a sphere of radius 0.010 (1) cm; precession photographs revealed monoclinic symmetry with systematic absences corresponding to the space group $P2_1/c$. The lattice parameters were determined in a least-squares refinement program, using 12 reflections within the angular range $30° < 2\theta < 45°$; the reflections were automatically centered on a Picker FACS-I four-circle diffractometer using Mo $K\alpha_1$ radiation (λ 0.709 30 Å). At 25 °C the lattice parameters are $a = 9.516$ (6), $b = 7.904$ (4), $c = 9.277$ (6) Å, and $\beta = 114.22$ (4)°, where the figures in parentheses represent the standard deviations in the last reported figure. The calculated density, with $Z = 4$, is 4.016 g cm^{-3}.

Diffraction intensities were measured using Zr filtered Mo $K\alpha$ radiation at a take-off angle of 3.0° with the diffractometer operating in the θ–2θ scan mode. Scans were made at 1° per min over 1.5° with allowance for dispersion and with 20-s background counts taken at both ends of the scan. Of the 1922 independent data investigated in the angular range $2\theta < 61°$, 1778 were considered observable according to the criterion $|F_o| > 1.54\sigma_F$, where σ_F is defined as $0.02 |F_o| + [C + k^2B]^{1/2}/2|F_o|Lp$; the total scan count is C, k is the ratio of scanning time to the total background time, and B is the total background count. Three reflections were systematically monitored and no variations in intensity greater than 4% were observed over the data collection period; the mean variation was very much smaller.

Intensity data were corrected for Lorentz and polarization effects, and absorption corrections[5] were applied for a spherical crystal with $\mu R = 0.85$. The maximum relative absorption correction applied was 2.0% of $|F_o|$.

Determination and Refinement of the Structure. On the basis of unit cell volumes (the unit cell of this new compound, 636 Å^3, was almost double that[6] of $Co_3(PO_4)_2$, 319 Å^3) the unit cell contents $Co_{12}P_8O_{32}$ (for $Z = 4$) were used in the direct methods crystallographic program MULTAN.[7] The five strongest peaks in the electron density map produced by MULTAN corresponded to three cobalt and two phosphorus atoms. Least-squares refinement of these cation positions and subsequent difference Fourier syntheses brought out a total of nine oxygen positions corresponding to the empirical formula $Co_3(PO_4)_2 \cdot H_2O$. We had no success in locating the hydrogen atoms using difference maps.

Three cycles of full-matrix least-squares refinement[8] using the positional parameters of these fourteen atoms, a $1/\sigma^2$ weighting scheme, zerovalent scattering factors[9] for Co, P, and O, isotropic temperature factors, and corrections for secondary extinction and anomalous dispersion yielded a residual $R = 0.064$ and a weighted residual $R_w = 0.086$. The anisotropic refinement, based on a data:parameter ratio of 13 with 128 independently varied parameters, yielded a final $R = 0.048$ and $R_w = 0.065$ for the observed data. In the final refinement, the maximum extinction correction[10] was 12% of $|F_o|$ for the $\bar{2}13$ reflection.

Results and Discussion

Table II presents the final atomic coordinates and anisotropic thermal parameters. There are three unique cobalt atoms; two lie in the centers of distorted octahedra and the third in a distorted five-coordinated trigonal bipyramid. Table III lists the bond distances and angles as well as polyhedral edge lengths for the three cobalt atoms. The standard deviations for all distances and angles were computed by the

Table II. Fractional Atomic Coordinates and Anisotropic Thermal Parameters^a

	10^4x	10^4y	10^4z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co(1)	2397.3 (8)	912.6 (9)	464.1 (8)	0.62 (3)	0.48 (3)	0.83 (3)	0.03 (2)	0.33 (2)	−0.02 (2)
Co(2)	1314.9 (8)	1140.2 (8)	1087.4 (8)	0.75 (3)	0.45 (3)	0.78 (3)	0.00 (2)	0.35 (2)	0.04 (2)
Co(3)	5722.7 (8)	1825.6 (8)	321.4 (8)	0.77 (3)	0.32 (3)	0.91 (3)	0.04 (2)	0.47 (2)	−0.04 (2)
P(1)	1213 (1)	4669 (1)	2672 (1)	0.61 (4)	0.26 (4)	0.72 (4)	−0.02 (3)	0.40 (3)	0.00 (3)
P(2)	4928 (1)	128 (1)	3008 (1)	0.53 (4)	0.29 (4)	0.71 (4)	0.02 (3)	0.35 (3)	−0.01 (3)
O(1)	1434 (4)	3756 (4)	1325 (4)	1.09 (13)	0.43 (12)	0.96 (12)	−0.06 (10)	0.65 (11)	−0.18 (10)
O(2)	7900 (4)	1354 (5)	1879 (4)	0.88 (13)	0.51 (13)	1.13 (13)	0.03 (10)	0.40 (11)	0.13 (10)
O(3)	498 (4)	103 (5)	2788 (4)	0.72 (12)	0.81 (13)	1.10 (13)	−0.03 (10)	0.52 (11)	−0.08 (10)
O(4)	1756 (4)	3470 (5)	4113 (4)	1.15 (13)	0.34 (12)	0.85 (13)	0.15 (10)	0.45 (11)	0.26 (10)
O(5)	4627 (4)	3403 (4)	1168 (4)	0.83 (13)	0.37 (12)	0.82 (12)	−0.14 (10)	0.28 (10)	−0.14 (10)
O(6)	3363 (4)	725 (5)	2918 (4)	0.52 (12)	0.93 (13)	1.03 (13)	0.11 (10)	0.40 (10)	−0.05 (11)
O(7)	4896 (4)	−46 (4)	1357 (4)	1.00 (13)	0.33 (12)	0.74 (12)	−0.23 (9)	0.53 (10)	−0.14 (9)
O(8)	6240 (4)	1307 (5)	4074 (4)	0.72 (12)	0.36 (12)	0.89 (12)	−0.09 (9)	0.38 (10)	−0.10 (9)
O(9)	8923 (4)	3468 (5)	4482 (4)	0.94 (13)	0.69 (13)	1.08 (13)	0.04 (10)	0.63 (11)	0.06 (10)

^{a} Numbers in parentheses are estimated standard deviations in the last significant figure.

Table III. Bond Distances, Polyhedral Edge Lengths, and Bond Angles for Cobalt Polyhedra

(i) Interatomic Distances, Å[a]

Co(1)–O(3)	2.013	Co(2)–O(6)	2.012	Co(3)–O(5)	1.976
Co(1)–O(5)	2.075	Co(2)–O(4)	2.056	Co(3)–O(7′)	1.993
Co(1)–O(4)	2.103	Co(2)–O(1)	2.070	Co(3)–O(2)	2.008
Co(1)–O(1)	2.120	Co(2)–O(9)	2.159	Co(3)–O(8)	2.049
Co(1)–O(6)	2.143	Co(2)–O(9′)	2.163	Co(3)–O(7)	2.079
Co(1)–O(8)	2.209	Co(2)–O(3)	2.177		
Co(1) polyhedron		Co(2) polyhedron		Co(3) polyhedron	
O(3)–O(4)	2.960	O(6)–O(4)	3.271	O(5)–O(7′)	3.677
O(3)–O(1)	3.148	O(6)–O(1)	3.001	O(5)–O(2)	3.315
O(3)–O(6)	2.714	O(6)–O(9)	2.973	O(5)–O(8)	2.927
O(3)–O(8)	3.443	O(6)–O(3)	2.714	O(5)–O(7)	2.728
O(5)–O(4)	2.993	O(4)–O(1)	2.804	O(7′)–O(2)	3.245
O(5)–O(1)	3.102	O(4)–O(9)	2.933	O(7′)–O(8)	3.037
O(5)–O(6)	2.826	O(4)–O(9′)	2.843	O(7′)–O(7)	2.598
O(5)–O(8)	2.410	O(1)–O(9′)	2.884	O(2)–O(8)	3.041
O(4)–O(1)	2.804	O(1)–O(3)	3.447	O(2)–O(7)	2.904
O(4)–O(6)	3.099	O(9)–O(9′)	3.051	O(8)–O(7)	4.119
O(1)–O(8)	3.115	O(9)–O(3)	2.704		
O(6)–O(8)	3.095	O(9′)–O(3)	3.015		

(ii) Angles, deg[b]

Co(1) polyhedron		Co(2) polyhedron		Co(3) polyhedron	
O(3)–Co(1)–O(4)	91.9	O(6)–Co(2)–O(4)	107.1	O(5)–Co(3)–O(7′)	135.8
O(3)–Co(1)–O(1)	99.2	O(6)–Co(2)–O(1)	94.6	O(5)–Co(3)–O(2)	112.6
O(3)–Co(1)–O(6)	81.5	O(6)–Co(2)–O(9)	90.8	O(5)–Co(3)–O(8)	93.3
O(3)–Co(1)–O(8)	109.2	O(6)–Co(2)–O(3)	80.7	O(5)–Co(3)–O(7)	84.3
O(5)–Co(1)–O(4)	91.5	O(4)–Co(2)–O(1)	85.6	O(7′)–Co(3)–O(2)	108.4
O(5)–Co(1)–O(1)	95.4	O(4)–Co(2)–O(9)	88.2	O(7′)–Co(3)–O(8)	97.4
O(5)–Co(1)–O(6)	84.1	O(4)–Co(2)–O(9′)	84.7	O(7′)–Co(3)–O(7)	79.3
O(5)–Co(1)–O(8)	68.4	O(1)–Co(2)–O(9′)	85.8	O(2)–Co(3)–O(8)	97.1
O(4)–Co(1)–O(1)	83.2	O(1)–Co(2)–O(3)	108.5	O(2)–Co(3)–O(7)	90.5
O(4)–Co(1)–O(6)	93.7	O(9)–Co(2)–O(9′)	89.8	O(8)–Co(3)–O(7)	172.3
O(1)–Co(1)–O(8)	92.0	O(9)–Co(2)–O(3)	77.2		
O(6)–Co(1)–O(8)	90.6	O(9′)–Co(2)–O(3)	88.0		
O(3)–Co(1)–O(5)	165.3	O(6)–Co(2)–O(9′)	168.2		
O(4)–Co(1)–O(8)	158.9	O(4)–Co(2)–O(3)	163.6		
O(1)–Co(1)–O(6)	176.9	O(1)–Co(2)–O(9)	172.7		

[a] Esd for Co–O distances 0.004 Å; for O–O distances 0.005 Å. [b] Esd for O–Co–O angles 0.1°.

function and error program ORFFE.[11]

Co(1) and Co(2) are coordinated by six oxygen atoms at average distances of 2.111 and 2.106 Å, respectively; Co(3) is coordinated by five oxygens at an average distance of 2.021 Å. The two average cobalt–oxygen distances for the six-coordinated cations agree rather well with the average distance of 2.125 Å found[6] for six-coordinated cobalt in $Co_3(PO_4)_2$ and the average distance for the five-coordinated cation agrees with the average of 2.045 Å for the fivefold cobalt in the anhydrous phosphate. This is quite interesting since the five-coordinated polyhedron in $Co_3(PO_4)_2$ consists of four short bonds and a longer one at 2.229 Å, while in the hydrate the bond lengths are more uniform. Aside from this close similarity in the average bond lengths about the divalent cobalt ion, there is no correspondence between the two structures.

The two phosphate tetrahedra have average bond lengths of 1.534 Å (−0.011, +0.006 Å) and 1.529 Å (−0.010, +0.012 Å), respectively, and average bond angles of 109.5° (−3.1, +3.1°) and 109.4° (−6.0, +2.7°). Table IV lists the bond lengths and angles and edge lengths for the phosphate tetrahedra. Inspection of the edge lengths and bond angles and comparison of the three distortion indices[12] for each of the two tetrahedra indicates a greater distortion in the P(2) tetrahedron which, as we shall see, is involved in edge sharing to a cobalt polyhedron.

The five-coordinated Co(3) cations form dimers by sharing an O(7)–O(7′) edge across a center of symmetry. The Co–Co distance in the dimer is 3.136 Å. The Co(2) octahedra are bridged by a pair of water oxygens (O(9)) about a center of symmetry to form an edge-shared unit with a Co(2)–Co(2) distance of 3.062 Å. Each Co(2) octahedron then shares the O(1)–O(4) edge with a Co(1) octahedron, thus forming the network illustrated in Figure 1, a projection of a part of the structure onto the *ab* plane. In this plane, the Co(1)–Co(2) distance is 3.059 Å. In addition, each Co(1) and Co(2) edge share through O(3) and O(6) in a direction roughly perpendicular to the *ab* plane with a Co(1)–Co(2) distance of 3.019 Å. This is shown in Figure 2, which contains all of the edge-sharing linkages between Co(1) and Co(2) atoms. Each Co(1) shares two oxygens O(5) and O(8), respectively, with a Co(3) in two different dimers (see Figure 1). Although not

Table IV. Bond Distances, Polyhedral Edge Lengths, and Bond Angles for the Phosphate Tetrahedra[a]

(i) Interatomic Distances, Å[a]

P(1)–O(1)	1.525	P(2)–O(7)	1.519
P(1)–O(2)	1.535	P(2)–O(6)	1.526
P(1)–O(3)	1.537	P(2)–O(5)	1.530
P(1)–O(4)	1.540	P(2)–O(8)	1.541
P(1) polyhedron		P(2) polyhedron	
O(1)–O(2)	2.547	O(7)–O(6)	2.506
O(1)–O(3)	2.527	O(7)–O(5)	2.466
O(1)–O(4)	2.479	O(7)–O(8)	2.538
O(2)–O(3)	2.459	O(6)–O(5)	2.524
O(2)–O(4)	2.521	O(6)–O(8)	2.530
O(3)–O(4)	2.496	O(5)–O(8)	2.410

(ii) Angles, deg[b]

O(1)–P(1)–O(2)	112.7	O(7)–P(2)–O(6)	110.8
O(1)–P(1)–O(3)	111.3	O(7)–P(2)–O(5)	107.9
O(1)–P(1)–O(4)	107.9	O(7)–P(2)–O(8)	112.1
O(2)–P(1)–O(3)	106.4	O(6)–P(2)–O(5)	111.3
O(2)–P(1)–O(4)	110.2	O(6)–P(2)–O(8)	111.1
O(3)–P(1)–O(4)	108.4	O(5)–P(2)–O(8)	103.4

[a] Esd for P–O distances 0.004 Å; for O–O distances 0.005 Å. [b] Esd for O–P–O angles 0.2°.

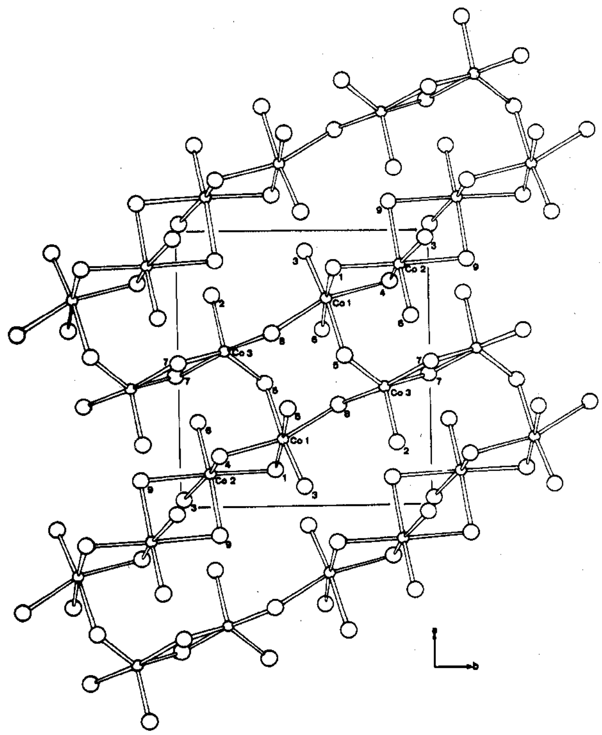

Figure 1. A projection of part of the structure onto the *ab* plane centered about 1/2 1/2 0. Cobalt atoms are represented by the smaller circles and oxygen atoms by the larger. The unit cell is outlined.

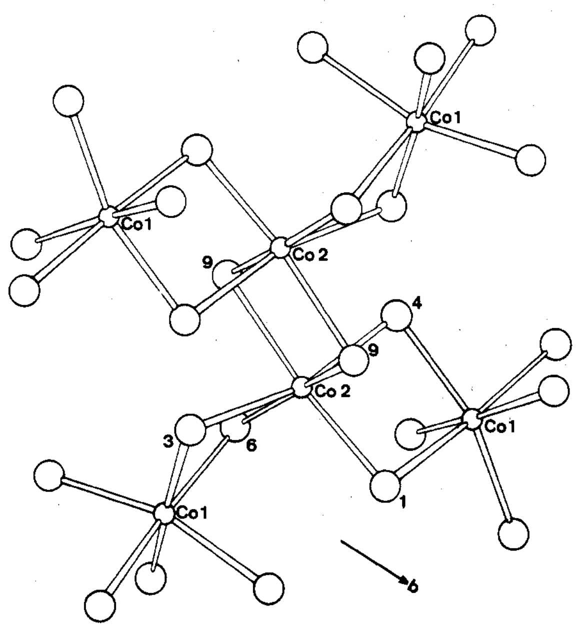

Figure 2. A projection of part of the structure illustrating the edge-sharing linkages between Co(1) and Co(2) polyhedra. Figure 2 is roughly perpendicular to Figure 1 (the *ab* plane); the *b* direction is indicated.

illustrated, this O(5)–O(8) edge is also shared with a P(2) tetrahedron which then connects through corner sharing to symmetry-related nets above and below the plane illustrated in Figure 1.

As we were not able to locate the hydrogen atoms directly and since it is possible to postulate a nonhydrate formula for this composition, e.g., $Co_3(HPO_4)(PO_4)(OH)$, which satisfies mass and charge balance, we should like to offer the following argument for our formulation. Oxygens 1 through 4 form the P(1) tetrahedron while oxygens 5 through 8 form the P(2) tetrahedron. O(9) is not bonded to a phosphorus atom but

Table V. Bond Distances, Bond Angles, and Polyhedral Edge Lengths for Oxygen Polyhedra

	Distance, Å[a]	Angle, deg[b]	Edge length, Å[c]
(i) O(1) Polyhedron			
O(1)–P(1)	1.525		
O(1)–Co(2)	2.070		
O(1)–Co(1)	2.120		
P(1)–O(1)–Co(2)		122.5	3.162
P(1)–O(1)–Co(1)		141.9	3.450
Co(2)–O(1)–Co(1)		93.8	3.059
(ii) O(2) Polyhedron			
O(2)–P(1)	1.535		
O(2)–Co(3)	2.008		
P(1)–O(2)–Co(3)		130.0	3.217
(iii) O(3) Polyhedron			
O(3)–P(1)	1.537		
O(3)–Co(1)	2.013		
O(3)–Co(2)	2.177		
P(1)–O(3)–Co(1)		141.2	3.353
P(1)–O(3)–Co(2)		122.1	3.265
Co(1)–O(3)–Co(2)		92.1	3.019
(iv) O(4) Polyhedron			
O(4)–P(1)	1.540		
O(4)–Co(2)	2.056		
O(4)–Co(1)	2.103		
P(1)–O(4)–Co(2)		124.0	3.184
P(1)–O(4)–Co(1)		138.6	3.414
Co(2)–O(4)–Co(1)		94.7	3.059
(v) O(5) Polyhedron			
O(5)–P(2)	1.530		
O(5)–Co(3)	1.976		
O(5)–Co(1)	2.075		
P(2)–O(5)–Co(3)		132.4	3.212
P(2)–O(5)–Co(1)		96.0	2.703
Co(3)–O(5)–Co(1)		116.6	3.447
(vi) O(6) Polyhedron			
O(6)–P(2)	1.526		
O(6)–Co(2)	2.012		
O(6)–Co(1)	2.143		
P(2)–O(6)–Co(2)		132.6	3.246
P(2)–O(6)–Co(1)		133.1	3.375
Co(2)–O(6)–Co(1)		93.1	3.019
(vii) O(7) Polyhedron			
O(7)–P(2)	1.519		
O(7)–Co(3)	1.993		
O(7)–Co(3′)	2.079		
P(2)–O(7)–Co(3)		136.4	3.265
P(2)–O(7)–Co(3′)		122.8	3.171
Co(3)–O(7)–Co(3′)		100.7	3.136
(viii) O(8) Polyhedron			
O(8)–P(2)	1.541		
O(8)–Co(3)	2.049		
O(8)–Co(1)	2.209		
P(2)–O(8)–Co(3)		118.4	3.095
P(2)–O(8)–Co(1)		90.4	2.703
Co(3)–O(8)–Co(1)		119.2	3.673
(ix) O(9) Polyhedron			
O(9)–Co(2)	2.159		
O(9)–Co(2′)	2.163		
Co(2)–O(9)–Co(2)		90.2	3.062

[a] Esd 0.004 Å. [b] Esd 0.2°. [c] Esd 0.005 Å.

to two Co(2) polyhedra. The question is: should O(9) be considered a water or a hydroxyl oxygen?

Table V presents the relevant bond angles and distances about each of the oxygen atoms. Note that each oxygen except O(2) and O(9) is bonded to two cobalt and one phosphorus atom. O(2) bonds to a single cobalt and one phosphorus and O(9) bridges two cobalts. We have calculated the bond valences (in valence units, vu) about each of the *metal* atoms using Brown and Shannon's[13] empirical correlation of bond length and bond valence: $S = S_0(R/R_0)^{-N}$, where S = bond

Table VI. Individual Bond Strengths and Bond Strength Sums about Oxygen Atoms (in vu)

O(1):	P(1)	1.27
	Co(2)	0.37
	Co(1)	0.33
	$\Sigma = 1.97$	
O(2):	P(1)	1.25
	Co(3)	0.44
	$\Sigma = 1.69$	
O(3):	P(1)	1.24
	Co(1)	0.43
	Co(2)	0.29
	$\Sigma = 1.96$	
O(4):	P(1)	1.23
	Co(2)	0.39
	Co(1)	0.35
	$\Sigma = 1.97$	
O(5):	P(2)	1.29
	Co(3)	0.47
	Co(1)	0.37
	$\Sigma = 2.13$	
O(6):	P(2)	1.27
	Co(2)	0.43
	Co(1)	0.31
	$\Sigma = 2.01$	
O(7):	P(2)	1.26
	Co(3)	0.45
	Co(3)	0.37
	$\Sigma = 2.08$	
O(8):	P(2)	1.23
	Co(3)	0.39
	Co(1)	0.27
	$\Sigma = 1.89$	
O(9):	Co(2)	0.30
	Co(2)	0.30
	$\Sigma = 0.60$	

valence, R = bond length, and S_0, R_0, and N are empirically fit constants for a given atom. The values[13] of S_0, R_0, and N for Co^{2+} and P^{5+} are 0.333, 2.118, 5.0 and 1.25, 1.534, 3.2, respectively. Summing the individual bond strengths about the nine *oxygen* atoms (see Table VI) shows that, except for O(2) and O(9), the bond strength sums cluster about the expected value of 2.00 vu (−0.11, +0.13 vu; average of seven oxygens 2.00 vu). O(2) has a bond strength sum of 1.68 and O(9) of 0.60 vu. This, of course, indicates that two hydrogens are bonded to O(9) and implies hydrogen bonding to O(2). In fact, inspection of the *interpolyhedral* oxygen–oxygen distances (oxygen atoms not sharing the same cation) shows that each O(9) has two O(2) atoms at distances of 2.755 and 2.763 Å; the next longest oxygen–oxygen distance of this type is 2.954 Å. The value 2.7 Å is just the oxygen–oxygen distance expected for a slightly strained hydrogen bond.[14] The bond strength of the *hydrogen bond* can be estimated as 0.20 vu[14] leaving a bond strength of 0.80 vu for the O–H bond. Thus O(9) (the water oxygen) will have a total bond strength sum of 2.20 vu and O(2) (the hydrogen bond acceptor) a sum of 2.08 vu.

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Registry No. $Co_3(PO_4)_2 \cdot H_2O$, 60305-65-9.

Supplementary Material Available: A table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Sterically Hindered Solvent Extractants. 2. A Neutron-Diffraction Study of the Di-*tert*-butylphosphinic Acid Dimer Showing Strong Asymmetric Hydrogen Bonding[1]

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Di-*tert*-butylphosphinic acid, $[(CH_3)_3C]_2PO(OH)$, is shown to be dimeric in the solid state with two acid molecules linked together by strong linear, 2.486 (9) Å, asymmetric hydrogen bonds forming an eight-membered centrosymmetric ring (**1**). The two O–H distances in the asymmetric H bond are 1.114 (15) and 1.372 (14) Å, the primary O–H being considerably lengthened. The molecule crystallizes in the monoclinic space group, $P2_1/c$, with unit cell parameters a = 8.979 (6), b = 13.119 (9), c = 10.576 (7) Å, β = 118.03 (3)°, and Z = 4. The structure was solved using the heavy-atom coordinates of the previously determined x-ray model and refined using 1001 three-dimensional neutron data by Fourier and full-matrix least-squares techniques to R_F = 0.048 for 525 reflections where $F_o > 3\sigma(F_o)$. The P–O bond lengths are P–O(1) = 1.531 (7) Å and P–O(2) = 1.518 (9) Å.

Introduction

Di-*tert*-butylphosphinic acid, $[(CH_3)_3C]_2PO(OH)$, H-[Dt-BP] hereafter, is part of a wide class of sterically hindered organophosphorus solvent extractors of lanthanide and actinide metal ions which show a great selectivity of metal ion extraction.[3] For example, the $[UO_2^{2+}]$ ion is extracted by H[Dt-BP] with an efficiency which is 10^7 greater than for Th(IV) ions under the same pH, diluent, and temperature conditions.[4] Recently, we have undertaken the study of the structural characteristics of several of these extractants in order to observe possible correlations between structure and selectivity.

Previously,[5] we have shown that H[Dt-BP] exists in the crystalline state as a discrete dimer, the only discrete dimeric R_2POOH acid to be described to date. The x-ray model was ambiguous as to the position of the hydrogen atoms linking the two halves of the dimer. Fourier maps derived from the x-ray data showed an extended cylindrical trough of electron density joining the two nonequivalent oxygen atoms of the eight-membered ring but did not reliably establish whether