

## The Local Structure of Tetrahedral Co(III): A Detailed Crystal Structure Investigation of $K_5Co^{III}W_{12}O_{40} \cdot 20H_2O$

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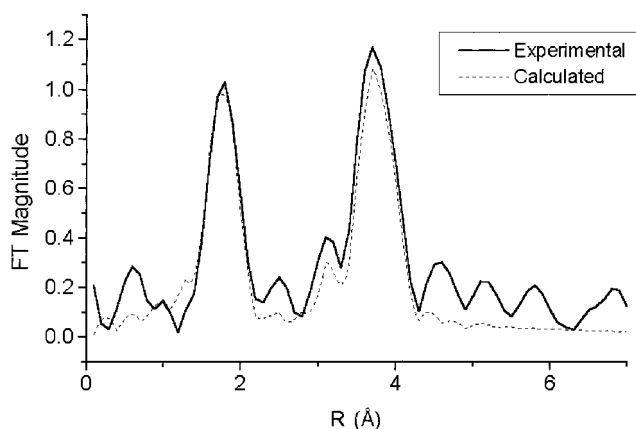
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Heteroatom-substituted aluminophosphates have attracted considerable attention in recent years due to their wide range of substitution chemistry, leading to the production of solid catalysts, with a range of functionality.<sup>1–3</sup> Substitution of certain divalent ions, for example Co(II) into Al(III) sites of an aluminophosphate (the so-called CoAlPO's), not only introduces strong acid properties, but also these ions can be raised to a higher oxidation state (Co(III)) by calcination in oxygen—a process typically used to remove the occluded organic template molecule employed in the synthesis of the materials.

In a few recent papers it has been argued that Co(III) ions, tetrahedrally linked via oxygens to phosphorus groups that constitute the framework of microporous materials, play a crucial role in the catalytic action exhibited by the so-called CoAlPO's.<sup>4,5</sup> Such reactions include the oxidation of alkanes and alkenes in the presence of air or hydroperoxides.<sup>6–10</sup>

X-ray absorption spectroscopic evidence offers convincing proof that Co(II) ions initially present in various CoAlPO structures may be raised, by calcining in oxygen for example, to the Co(III) state (to various degrees), without exclusion of the transition metal ions from the framework.<sup>11–18</sup> But other measurements, notably those



**Figure 1.** Fourier transform of the Co K-edge EXAFS data. The solid line shows the experimental data and the dashed curve represents the calculated data derived from analyzing the EXAFS data. The final average Co–O and Co–W distances obtained from the analysis are 1.79 Å with a Debye–Waller factor ( $\sigma^2$ ) of 0.003, and 3.51 Å with a Debye–Waller factor of 0.005, respectively.

using ESR spectroscopy indicate that in certain CoAlPO structures, there is little evidence for the existence of Co(III) framework ions.<sup>19–22</sup>

We have found it convenient to track the conversion of Co(II) to Co(III) ions, and vice versa, not only by the shift of the X-ray K-absorption edge but also from the EXAFS derived Co–O bond distances. We find, typically, that the spatially averaged Co(II)–O bond distance is 1.93 Å (close to that found in  $CoAl_2O_4$ ), whereas the averaged Co(III)–O distance in the completely calcined material is close to 1.82 Å. Indeed with such information the average fraction of Co ions in the (II) or (III) oxidation states, in a given zeotypic structure taken up by the AlPO in question, can be estimated.<sup>13</sup> As this profoundly influences the catalytic performance of the CoAlPO, either as a solid acid catalyst or as a selective oxidation one, it is important to determine unequivocally, by X-ray crystallography, the Co–O bond distance for a given, well-defined example which can be prepared in either the Co(II) or Co(III) states. Such an example is presented by the cobalt containing heteropolytungstate of the type  $K_5CoW_{12}O_{40} \cdot 20H_2O$ .<sup>23</sup>

Baker and co-workers<sup>23</sup> reported the synthesis of this material from which pure, stable single crystals were isolated. The crystal structure derived from this earlier study of  $K_5Co^{III}W_{12}O_{40} \cdot 20H_2O$  has a Co–O bond distance of 1.88 Å.<sup>24</sup> This value is found to be signifi-

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**Table 1. Crystallographic Data for  $K_5[CoW_{12}O_{40}] \cdot 20H_2O$** 

$T$ (K)	150
formula	$K_5[CoW_{12}O_{40}] \cdot 20H_2O$
fw, g mol <sup>-1</sup>	3460.95
$a$ , Å	18.937(3)
$c$ , Å	12.484(2)
$V$ , Å <sup>3</sup>	3877.1(11)
symmetry	Hexagonal
space group	$P3(1)$
$\lambda$ , Å	0.71073
no. of unique reflections	15171
no. of variables	544
R1 For $I > 2\sigma(I)$	0.0539
wR2 For $I > 2\sigma(I)$	0.1235
R1 for all data	0.1196
wR2 for all data	0.1519

cantly greater (by  $\sim 0.08$  Å) than those derived using Co K-edge EXAFS (for which we note that the error associated with determining bond distance is  $\sim 0.02$  Å) and by applying the bond valence sum model (BVS model) to tetrahedral Co(III). The Fourier transform of the experimental and calculated EXAFS data are shown in Figure 1. In addition, upon closer inspection of the earlier structure solution<sup>24</sup> we found that some of the W–O separations were far shorter (in the region of 1.35 Å) than one would expect.

In view of the importance of determining accurate Co(III)–O bond lengths for tetrahedrally coordinated systems, we have reinvestigated the structure of  $K_5Co^{III}W_{12}O_{40} \cdot 20H_2O$  using single-crystal diffraction technique. The material was synthesized using a well-established method,<sup>25</sup> which produced yellow/green crystals with dimensions of  $\sim 200 \times 20 \times 20$   $\mu\text{m}$ .

The structure was solved and refined using the SHELX-97<sup>26</sup> suite of programs. In the earlier report,<sup>24</sup>

the structure of this material was solved using the space group  $P6222$ . However, we could not obtain any satisfactory structure solution when we attempted to solve the structure with the new data set using this space group. We identified the space group to be  $P3(1)$ . Crystallographic details are given in Table 1. The final  $R$  factor of our refinement was 5.5%, significantly lower than the one reported earlier (19.4%).<sup>24</sup>

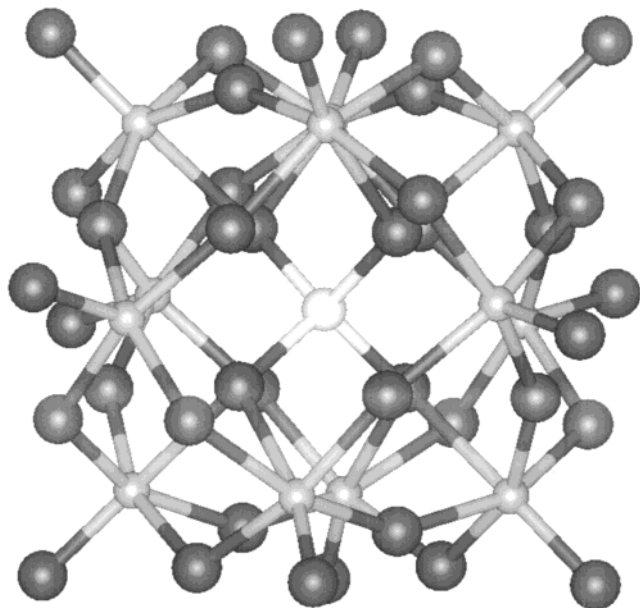
We were able to identify the W, Co, and non-water O atom positions without much difficulty, 2 of the 5 potassium ions and 12 of the 20 water molecules. It is likely that the other 3  $K^+$  ions and 8 water molecules are considerably disordered, since we did not find any clear electron density in the difference Fourier representing these atoms. As a result of the presence of disordered species the  $R$  factor remained above 5%. Attempts to assign positions to additional atoms led to an unstable refinement and atoms with unrealistic temperature factors. The oxygen atoms associated with water molecules were refined isotropically, and all other atoms were refined with anisotropic temperature factors. No other restraints were required. Fractional coordinates are given in Table 2. A selection of bond distances derived from diffraction are given in Table 3, and the final structure is shown in Figure 2.

The most important aspect of this work is the Co–O bond distances. Our refinement shows that the cobalt is in a slightly distorted tetrahedral environment with an average Co–O bond distance of  $\sim 1.79$  Å, considerably shorter than the one (1.88 Å) reported earlier. Terminal W–O distances are in the region 1.69–1.72 Å and the bridging oxygens are  $\sim 1.9$  Å. Furthermore,

**Table 2. Fractional Coordinates and U Values for  $K_5[CoW_{12}O_{40}] \cdot 20H_2O$** 

atom <sup>a</sup>	$x$	$y$	$z$	$U$	atom <sup>a</sup>	$x$	$y$	$z$	$U$
K1	0.6292(3)	0.2581(3)	−0.1248(4)	0.0354(10)	O20	0.4676(9)	−0.1772(8)	0.2871(12)	0.031(3)
K2	0.3706(3)	−0.2587(3)	−0.1240(4)	0.0371(11)	O21	0.6219(10)	0.2246(8)	0.6667(10)	0.033(4)
W1	0.58239(6)	0.14952(5)	0.17573(7)	0.0334(2)	O22	0.6032(10)	0.2235(9)	0.0830(12)	0.041(4)
W2	0.56723(6)	0.14953(5)	0.57632(7)	0.0332(2)	O23	0.5329(9)	−0.0939(8)	0.6505(12)	0.033(3)
W3	0.43285(6)	−0.14960(5)	0.57640(7)	0.0338(2)	O24	0.3969(10)	−0.2247(9)	0.0834(12)	0.041(4)
W4	0.41755(6)	−0.14961(5)	0.17565(7)	0.0332(2)	O25	0.3529(9)	−0.1784(9)	0.4648(12)	0.033(3)
W5	0.62811(6)	−0.00873(6)	0.57355(8)	0.0349(2)	O26	0.3725(9)	−0.0938(8)	0.1007(12)	0.034(4)
W6	0.37191(6)	0.00870(6)	0.57362(8)	0.0349(2)	O27	0.3108(10)	0.0120(11)	0.0836(13)	0.044(4)
W7	0.36317(6)	−0.00878(6)	0.17837(8)	0.0347(2)	O28	0.3792(11)	−0.2240(9)	0.6680(12)	0.040(4)
W8	0.63684(6)	0.00879(6)	0.17831(8)	0.0346(2)	O29	0.2723(9)	−0.0934(9)	0.2552(13)	0.038(4)
W9	0.55323(6)	−0.15315(5)	0.38672(8)	0.0332(2)	O30	0.3790(10)	0.0652(9)	0.2876(12)	0.037(4)
W10	0.29367(5)	−0.15313(5)	0.36510(8)	0.0328(2)	O31	0.4157(9)	−0.0596(9)	0.2899(12)	0.034(3)
W11	0.44676(6)	0.15304(5)	0.38677(8)	0.0333(2)	O32	0.7005(11)	0.0123(11)	0.6668(15)	0.050(5)
W12	0.70634(5)	0.15308(5)	0.36526(8)	0.0332(2)	O33	0.2986(11)	−0.0114(11)	0.6665(14)	0.050(5)
Co1	0.50011(18)	0.00001(17)	0.3761(3)	0.0261(5)	O34	0.5853(8)	0.0628(8)	0.2903(13)	0.032(3)
O1	0.4199(10)	0.2239(9)	0.3543(13)	0.038(4)	O35	0.6878(11)	−0.0125(11)	0.0832(15)	0.051(5)
O2	0.4093(9)	−0.0657(8)	0.6127(11)	0.029(3)	O36	0.6275(10)	0.0929(10)	0.1011(11)	0.035(4)
O3	0.5912(10)	0.0661(9)	0.6123(12)	0.036(4)	O37	0.3121(9)	−0.0661(8)	0.4656(12)	0.031(3)
O4	0.5264(10)	−0.0671(9)	0.1399(11)	0.034(4)	O38	0.5228(9)	−0.0627(9)	0.4602(12)	0.034(3)
O5	0.4743(9)	0.0659(9)	0.1400(12)	0.034(3)	O39	0.3654(9)	0.0920(9)	0.4974(13)	0.039(4)
O6	0.6861(9)	0.0660(8)	0.4666(12)	0.031(3)	O40	0.4760(9)	0.0616(9)	0.4597(13)	0.037(4)
O7	0.5773(10)	−0.2262(9)	0.3564(13)	0.038(4)	O1S	0.4984(8)	−0.0012(9)	0.8169(10)	0.026(3)
O8	0.3152(9)	−0.2099(8)	0.2531(12)	0.032(3)	O2S	0.4997(10)	−0.0007(9)	−0.0655(11)	0.034(3)
O9	0.4755(8)	−0.2085(8)	0.4983(11)	0.028(3)	O3S	0.3480(12)	−0.1188(12)	−0.1386(15)	0.055(5)
O10	0.8052(9)	0.2250(9)	0.3968(14)	0.040(4)	O4S	0.5340(12)	−0.1165(12)	−0.1076(14)	0.052(5)
O11	0.5228(9)	0.2076(8)	0.4958(11)	0.029(3)	O5S	0.6520(12)	0.1176(12)	−0.1418(15)	0.054(5)
O12	0.6844(10)	0.2093(8)	0.2537(11)	0.032(3)	O6S	0.4644(12)	0.1177(12)	0.8909(15)	0.058(5)
O13	0.1963(9)	−0.2250(9)	0.3976(14)	0.041(4)	O7S	0.8684(16)	0.1317(16)	0.540(2)	0.084(7)
O14	0.4658(9)	0.0924(9)	0.6545(12)	0.034(4)	O8S	0.7357(15)	−0.1326(16)	0.212(2)	0.084(7)
O15	0.7287(8)	0.0929(8)	0.2557(13)	0.035(4)	O9S	0.742(3)	0.000(3)	−0.123(4)	0.155(13)
O16	0.6456(9)	0.1788(9)	0.4654(11)	0.030(3)	O10S	0.805(3)	−0.196(3)	0.043(4)	0.174(15)
O17	0.5333(9)	0.1784(9)	0.2882(11)	0.029(3)	O11S	0.801(2)	−0.004(3)	0.379(4)	0.159(14)
O18	0.6195(8)	−0.0668(8)	0.2864(11)	0.028(3)	O12S	0.259(4)	−0.003(4)	−0.120(5)	0.23(2)
O19	0.6333(9)	−0.0945(9)	0.4964(11)	0.030(3)					

<sup>a</sup> The oxygen atom labels ending with S are associated with water molecules.



**Figure 2.** Final structure of  $K_5[CoW_{12}O_{40}] \cdot 20H_2O$  derived from single-crystal X-ray diffraction: large white spheres, Co; smaller light gray spheres, W; large dark gray spheres, O. Neither the potassium nor water molecules are shown for clarity.

**Table 3. Selected Bond Distances Showing Co–O Distances and the Maximum and Minimum W–O Distances for Terminal (W–O<sub>t</sub>) and Bridging (W–O<sub>b</sub>) Bonds**

bond	<i>d</i> (Å)
Co–O1	1.7839
Co–O2	1.7865
Co–O3	1.7923
Co–O4	1.8017
Terminal W=O Bonds	
W–O <sub>t</sub> (min)	1.6874
W–O <sub>t</sub> (max)	1.7215
W–O <sub>t</sub> (average)	1.7055
Bridging W–O bonds (W–O–W)	
W–O <sub>b</sub> (min)	1.8549
W–O <sub>b</sub> (max)	1.9684
W–O <sub>b</sub> (av)	1.9207

the O–O separations are in the region of 2.6 Å.

The Co–O distance of 1.79 Å is very close to the one predicted by the BVS model (1.78 Å) as well as the Co–O distance derived from the analysis of the Co K-edge EXAFS data of this material (see Figure 1). This result has large implications for the correlation of the structure with catalytic properties. This fundamental parameter defining the precise coordination geometry will serve as a good model for estimating the fraction

of cobalt 2+ that has been oxidized to the 3+ state in the calcined cobalt containing aluminophosphates. In addition, this will allow us, now, to understand the redox properties of these solids.

### Experimental Section

In a typical synthesis<sup>25</sup> of  $K_5[CoW_{12}O_{40}] \cdot 20H_2O$ ,<sup>23</sup>  $Na_2WO_4 \cdot 2H_2O$  was dissolved in water and the pH of the solution adjusted to ~3.5 using acetic acid. The solution was heated to boiling and a second aqueous solution, of  $Co(C_3H_3O_2)_2 \cdot 4H_2O$ , was added. The mixture was heated for 15 min before addition of KCl. The mixture was then cooled, and the product was removed by filtration. The resultant solid was then heated to ~90 °C in 2 M  $H_2SO_4$  for ~5 min, and the solution was filtered to remove any undissolved impurities. This filtrate was heated to boiling before slowly adding solid  $K_2S_2O_8$ , with continuous stirring, until the solution turned to a gold color. Crystals of  $K_5[CoW_{12}O_{40}] \cdot 20H_2O$  were obtained upon cooling the above solution. The samples produced were yellow/green prismatic crystals with dimensions up to  $\sim 200 \times 20 \times 20 \mu m$ . The crystal used for the diffraction experiment was approximately  $100 \times 20 \times 20 \mu m$  and showed no obvious sign of defects.

Data were collected at the EPSRC Crystallography service in Southampton, using an Enraf Nonius Kappa CCD diffractometer fitted with the Nonius FR591 rotating anode X-ray generator. Indexing and data collection is done by the software package DENZO.<sup>27</sup> Scaling is performed by Scalepack and adsorption corrections calculated in Sortav.<sup>28,29</sup> The structure was then solved and refined using the SHELX-97 suite of programs.<sup>26</sup>

Room-temperature Co K-edge EXAFS data were collected at station 8.1 of the Daresbury Synchrotron Radiation source, which operates at 2 GeV with a typical current in the range of 130–250 mA. This station was equipped with Si (220) monochromator, ion chambers for incident and transmitted beam intensity, and a 13-element fluorescence detector. The data were analyzed using the suite of programs, viz, EXCALIB (converting the raw data to energy vs absorption coefficient), EXBROOK (for pre- and postedge background subtraction) and EXCURV98 (for detailed least-squares refinement), available at the Daresbury Laboratory.

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**Supporting Information Available:** Tables of CIF data for and ORTEP drawing of  $K_5Co^{III}W_{12}O_{40} \cdot 20H_2O$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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