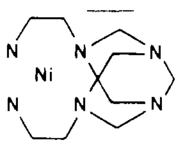

C

Ni(II) complex of semisepulchrate ligand prepared in this study, as well as the Co(III), Pt(IV), and Ni(II) complexes of sepulchrate,[8-10] contains methylenediamine linkages with secondary nitrogens. Therefore, methylenediamine groups containing secondary amines can be stabilized by coordination of the secondary nitrogens to a metal ion. However, the formation of C from $[Ni(semisep)]^{2+}$ indicates that the secondary nitrogens of methylenediamine groups are still reactive enough to produce tertiary nitrogens upon reaction with formaldehyde in the presence of free amines.

Acknowledgment. This work was supported by the Basic Research Institute Program (1984), Ministry of Education, Korea.

Registry No. $[Ni(semisep)](ClO_4)_2$, 98087-70-8; NH_3, 7664-41-7; CH_2O, 50-00-0; en, 107-15-3.

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Time of Flight Neutron Powder Rietveld Refinement of the $ZrKH(PO_4)_2$ Structure

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In a recent publication[1] we described the structure of $ZrKH(PO_4)_2$ as determined from Rietveld refinement of X-ray powder data. This compound is prepared by ion exchange of the parent α-zirconium phosphate, $Zr(HPO_4)_2{\cdot}H_2O$, followed by dehydration at 200 °C.[2] The structures of both the acid phosphate[3,4] and the half-exchanged potassium ion salt are layered. In the salt, the potassium ions are located exactly midway between the layers and are bonded to four $P-O^-$ type oxygens designated as O7 and O10. However, each of these oxygens bonds to two K^+ ions, the charge deficiency being compensated by protons. The location of the protons could not be determined from the X-ray data, but their positions were inferred from the structure.[1,5] This study was carried out in an effort to locate the protons precisely.

There was, however, another compelling reason for carrying out a neutron diffraction study. The structure of the subject compound was initially solved by Patterson and Fourier methods using 47 reflections that could be unambiguously indexed[5] in the X-ray powder pattern. This model was then refined by the X-ray Rietveld method. The procedures for solving structures from such minimal data sets have been described elsewhere.[6] There has been a certain amount of disagreement over the accuracy and validity of Rietveld refinement of X-ray data. This controversy centers around the falloff in intensities with increasing Bragg angle and the correspondence of experimental errors to refinement errors.[7-9] It was therefore of interest to compare the accuracy of the X-ray study with a detailed neutron diffraction study.

Table I. Neutron TOF Refinement Parameters for $ZrKH(PO_4)_2$

space group	*P*2/*c*
cell params	
a, Å	9.2208 (7)
b, Å	5.3280 (4)
c, Å	16.6336 (17)
β, deg	114.351 (11)
V, Å^3	744.47 (7)
Z	4
data range, μs	5275-20000
data range, Å	0.92-3.67
no. of contributing reflcns	971
no. of deg of freedom	2099
T, K	295

$R_{wp} = [\sum_i w_i[Y_i(\text{obsd}) - Y_i(\text{calcd})]^2/\sum_i w_i[Y_i(\text{obsd})]^2]^{1/2}$ 0.0242

$R_P = \sum_i[Y_i(\text{obsd}) - Y_i(\text{calcd})]/\sum_i[Y_i(\text{obsd}) - \text{bkgd}_i]$ 0.0702

$R_e = df^{1/2}/\sum_i w_i[Y_i(\text{obsd})]^2$ 0.0146

Table II. Positional Parameters for $ZrHK(PO_4)_2$

atom	*x*	*y*	*z*
Zr	0.7504 (15)	0.7729 (15)	0.9945 (9)
K1	0.5	0.0559 (57)	0.25
K2	0.0	-0.0740 (63)	0.25
P1	0.1715 (17)	0.7063 (19)	0.1176 (10)
P2	0.6632 (15)	0.2742 (33)	0.1115 (9)
O1	-0.0015 (16)	0.7709 (30)	0.0959 (11)
O2	0.2158 (15)	0.4938 (26)	0.0728 (9)
O3	0.2438 (17)	0.9480 (31)	0.0952 (12)
O4	0.6754 (13)	0.5260 (27)	0.0667 (8)
O5	0.5171 (15)	0.7634 (29)	0.9139 (8)
O6	0.7293 (15)	0.0559 (33)	0.0807 (10)
O7	0.2602 (14)	0.6969 (27)	0.2221 (8)
O10	0.2730 (14)	0.2907 (29)	0.2952 (8)
H1	0.2485 (35)	0.5108 (50)	0.2285 (19)

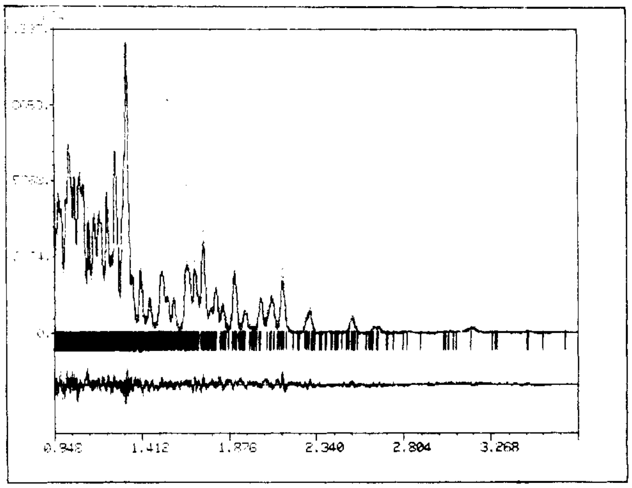

Figure 1. Plot of neutron intensity (counts) vs. *d* spacing (Å) for $ZrKH(PO_4)_2$. Observed data are represented by dots, calculated as the solid line. The lower plot is the difference. Vertical strikes indicate calculated Bragg peak positions.

Experimental Section

A neutron time of flight data set was collected on a sample of $ZrKH(PO_4)_2$ that had been loaded into a sealed vanadium can under an inert dry atmosphere. Data were taken on the special-environments powder diffractometer (SEPD) at the intense pulsed neutron source (IPNS), Argonne National Laboratory.[10] Data collection on the sample, about 5.2 cm^3, required 12 h. Data reduction was performed on data from the 90° data banks, and the X-ray Rietveld refined structural parameters[1] were used as the starting model. Refinement was carried out with a neutron Rietveld analysis program[11] in the *d*-spacing range of 3.67-0.92

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Table III. Important Bond Lengths (Å) and Angles (deg)

bond	av[a]	range
Zr–O	2.081 (43)	1.913 (20)–2.212 (16)
P1–O	1.544 (20)	1.501 (24)–1.588 (19)
P2–O	1.507 (32)	1.418 (18)–1.550 (19)
O7–H1	1.008 (31)	
O10–H1	1.565 (32)	
O7–O10 (short)	2.461 (21)	

angle	av[a]	range
O–Zr–O	88.9 (16)	81.0–95.5
O–P–O	109.2 (16)	102.7–121.7
O7–H1–O10	145.2 (28)	

K coord[b]	length	K coord[b]	length
K1–O3	2.744 (15)	K2–O1	2.688 (21)
K1–O5	2.834 (18)	K2–O6	2.974 (15)
K1–O7	2.814 (25)	K2–O7	2.895 (20)
K1–O10	2.794 (21)	K2–O10	3.019 (26)

[a] The esd of N observations is calculated as $[\sum|\text{av} - \text{obsd}|^2/N(N-1)]^{1/2}$. [b] All two contacts.

Å using a five-term refinable background function. No thermal diffuse scattering (TDS) background corrections were included in this function. No corrections were made for multiple scattering as the oscillatory nature of the background, characteristic of multiple scattering, was not observed. Refinement proceeded slowly until the [001] preferred orientation vector was assumed to have a Gaussian distribution about the axis of the sample. This preferred orientation factor is refinable as part of the least-squares technique. Refinement of better crystal and atom parameters now proceeded smoothly to convergence, at which stage a difference Fourier synthesis revealed the position of the hydrogen atom. Refinement of all parameters (including the hydrogen) was conducted to convergence, following which the non-hydrogen atoms were refined with anisotropic temperature factors.

Results and Discussion

Details of the refinement parameters are given in Table I while the positional parameters are contained in Table II. The final difference plot for the neutron Rietveld refinement is shown in Figure 1, and a summary of the bond distances and angles is given in Table III. Comparison of the results with those obtained in the X-ray study[1,5] reveals agreement within 3σ of the quoted esd's except for two K–O interatomic distances that exceed the 3σ criterion by about 10%. It should be remembered that the subject compound is layered so that the intensity data suffer from severe preferred orientation effects. Better handling of this error would undoubtedly improve matters considerably.

The hydrogen atom occupies a position between the P–O$^-$ (O7 and O10) groups, as predicted previously.[5] It is bonded to O7 at a distance of 1.0 Å and hydrogen bonds to O10 at 1.57 Å. The hydrogen bond angle is 145°. This positioning of the hydrogen atom makes O7 four-coordinate since it bridges two potassium ions as well as bonding to hydrogen and phosphorus. The arrangement is a highly distorted tetrahedron.

It appears from this study that the structure of an unknown compound can be deduced from a minimal data set (40–50 reflections) by using deconvoluted powder X-ray intensity data to obtain a starting model for both X-ray and neutron Rietveld refinement with satisfactory results. We are in the process of applying this technique to a variety of compounds.

Acknowledgment. IPNS is operated under the auspices of the U.S. Department of Energy to whom thanks are extended for the use of their facilities. This research was supported by Robert A. Welch Foundation Grant No. A673 and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also wish to thank J. D. Jorgensen and J.-E. Jorgensen for help with the data collection.

Registry No. $ZrKH(PO_4)_2$, 54408-13-8.

Supplementary Material Available: Listings of positional parameters and anisotropic temperature factors (1 page). Ordering information is given on any current masthead page.

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9-Iodo-*o*-carborane[1]

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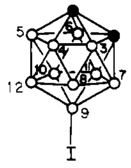
Although the synthesis of 9-iodo-*o*-carborane (**1**) has been described in the literature[3] we have experienced difficulty in making this useful intermediate in the synthesis of 9-alkyl-*o*-carboranes.[4] We describe here a simple modification of the published[3] procedure that gives high yields of pure **1**.



1

The published synthesis calls for treatment of *o*-carborane with I_2 and $AlCl_3$ in CCl_4 for 3 h.[3] We found that this procedure leads to a mixture of halogenated carboranes containing, along with the desired **1** (28%), 9-chloro-*o*-carborane (**2**, 13%), 9,12-dichloro-*o*-carborane (**3**, 11%), 9-chloro-12-iodo-*o*-carborane (**4**, 28%), and 9,12-diiodo-*o*-carborane (**5**, 20%). That chlorinated carboranes should be present was perhaps not unexpected given the report[6] that *o*-carborane could be chlorinated in the presence of CCl_4 and $AlCl_3$.

Compounds **2**, **3**, and **5** are known, and their physical and spectroscopic properties could be compared to those reported in the literature (**2**,[7] **3**,[9] **5**[3,7b,10]). Compound **4** is new and was identified by high-resolution mass spectrometry and ^{11}B NMR spectroscopy.

We found the composition of products not to vary with time, but reducing the temperature to 40 °C did increase the percentage of **1**, although the other halogenated carboranes were still present. We were finally successful in obtaining a high yield of pure **1** by combining low temperature with a change of solvent. Methylene chloride seemed less likely than CCl_4 to contribute a chlorine to the reaction pool, and this proved to be the case.[8] Treatment of *o*-carborane with iodine and $AlCl_3$ in CH_2Cl_2 gave **1** in good yield and high purity. Traces of **5** and a compound believed to be

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(1) Support for this work through Grant CHE 8318345 from the National Science Foundation is gratefully acknowledged. We also express our thanks to the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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