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**Is there any Zr in 'Na<sub>2</sub>NiZr(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>' or 'Na<sub>2</sub>CoZr(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>'?** By RICHARD E. MARSH, *A. A. Noyes Laboratory of Chemical Physics,\* California Institute of Technology, Pasadena, California 91125, USA*

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**Abstract**

The crystal structures of two isomorphous ionic conductors, reported as Na<sub>2</sub>MZr(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub> with *M* = Ni or Co, were originally described and refined in space group *P*1 [Gali, Byrappa & Gopalakrishna (1989). *Acta Cryst.* C45, 1667–1669]. Refinement in *P*1̄ is to be preferred, leading to lower *R*'s and to more satisfactory parameters. More important, the *P*1̄ refinements show that (1) there is no more than a small amount of Zr present in the crystals, (2) an additional proton is present, forming a very strong hydrogen bond between neighboring P<sub>2</sub>O<sub>7</sub> groups. Thus, the compounds are properly formulated as Na<sub>1-2x</sub>M<sub>1-x</sub>Zr<sub>x</sub>HP<sub>2</sub>O<sub>7</sub>, with *x* = 0.1 or less. The vacancies in the Na sites probably increase the ease of sodium-ion transport in these ionic conductors.

Recently, Gali, Byrappa & Gopalakrishna (1989; hereinafter, GBG) reported the crystal structures of two isomorphous ionic conductors, identified as Na<sub>2</sub>MZr(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub> with *M* = Ni or Co. The structures were described in the triclinic space group *P*1. For both compounds, however, the resulting structure (see GBG, Table 1 and Fig. 1) showed an approximate center of symmetry, relating pairs of Na, P and O atoms but also relating Zr to the *M* atom, Ni or Co. Another surprising feature was the very large *B*<sub>eq</sub> values for the Zr atom in both compounds (GBG, Table 1), which suggested that the occupancy of the Zr site might not correspond to a full Zr atom; conceivably it might be equivalent to that of the *M* site (which showed moderate *B*<sub>eq</sub>'s in both compounds), in which case the center of symmetry might be exact. Accordingly, further refinement in the centrosymmetric space group *P*1̄ seemed appropriate.

Structure factors for both compounds were obtained from SUP 52029; starting parameters were from GBG, symmetrized so as to conform to *P*1̄. The pair of sites *M*, Zr was presumed to be fully occupied by *M* (Ni or Co). Refinement was by full-matrix minimization of  $\sum w(F_o^2 - F_c^2)^2$ ; since individual values of  $\sigma(F_o^2)$  were not available from SUP 52029, weights *w* were assigned according to Hughes (1941; see also Marsh & Schomaker, 1979). Initial refinement with all atoms anisotropic proceeded routinely to *R*'s of 0.037 for the Ni compound and 0.035 for Co, with 101 parameters in each case (including one for

secondary extinction); the corresponding *R*'s for the *P*1 structures of GBG were 0.041 and 0.046, with (apparently) 126 parameters. However, for both compounds the displacement parameters *U*<sub>*ij*</sub> for the Na atoms were highly anisotropic, and difference maps strongly suggested that these atoms occupy more than one site. Accordingly, Na atoms were introduced into two separate sites, about 0.5 Å apart, with isotropic *B*'s; a site distribution factor *P*<sub>1</sub> was included. For both compounds there was a small but significant improvement in *R* – to 0.034 for the Ni compound and to 0.033 for Co.

But there was now a bit of a problem: replacing a Zr<sup>IV</sup> atom with Ni<sup>II</sup> (or Co<sup>II</sup>) leads to a charge imbalance, an additional positive charge (besides Na<sup>+</sup> and Co<sup>2+</sup>) being needed to counterbalance the P<sub>2</sub>O<sub>7</sub><sup>2-</sup> ion. This additional charge undoubtedly comes from a proton. Among the interionic O···O contacts is an extremely short one, at 2.44 Å for both compounds, between O(1) of one P<sub>2</sub>O<sub>7</sub> ion and O(7) of an ion related by translation along *c* (see Fig. 1). This distance is about 0.4 Å shorter than the normal van der Waals separation – so short that there must be a proton in between (there is no other cation bridging the two atoms). Indeed, difference maps for both the Ni and Co compounds showed peaks of height about 0.6 e Å<sup>-3</sup>, midway between these two O atoms and somewhat elongated along the O···O line. (These were not the largest peaks in the maps, which ranged up to 1.00 e Å<sup>-3</sup> for the Ni compound and to 0.88 e Å<sup>-3</sup> for the Co compound. But they were the largest peaks that were not closely associated with *M*, Na or P.) Including the H atom in a fixed position midway between the O's led to very slight decreases in *R*, which were now 0.033 for both compounds. Final coordinates for this model are given in Tables 1 and 2.†

In order to check on the occupancy of the *M* sites, additional refinements were carried out with the addition of a second 'population' parameter, *P*<sub>2</sub>, representing the fractional occupancy of the sites by Ni or Co, the amount of Zr being (1 - *P*<sub>2</sub>). At the same time, the population factors of the two different Na<sup>+</sup> sites were allowed to refine independently (since the total amount of Na<sup>+</sup> must

† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53149 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

\* Contribution No. 8100.

Table 1. Coordinates, Ni compound

$x, y, z$  and  $U_{eq}^* \times 10^4$ . Space group,  $P\bar{1}$ . Cell dimensions:  $a = 6.461$  (3),  $b = 7.257$  (4),  $c = 6.501$  (3) Å,  $\alpha = 123.24$  (1),  $\beta = 91.95$  (1),  $\gamma = 93.79$  (1)° (GBG).

	$x$	$y$	$z$	$U_{eq}$ or $B$
Ni	3571 (1)	1082 (1)	3942 (1)	79 (1)
P(1)	-3816 (2)	3640 (2)	1987 (2)	75 (2)
P(2)	-1410 (2)	2191 (2)	4749 (2)	75 (2)
O(1)	-2967 (5)	2189 (5)	-588 (6)	118 (8)
O(2)	-5794 (5)	2498 (6)	2053 (6)	124 (7)
O(3)	-3865 (5)	5975 (5)	2683 (6)	117 (6)
O(4)	-2075 (5)	3757 (5)	3879 (6)	123 (6)
O(5)	394 (5)	1040 (5)	3333 (6)	128 (7)
O(6)	-3296 (5)	514 (5)	4139 (6)	100 (6)
O(7)	-907 (5)	3748 (5)	7536 (5)	109 (8)
Na(1)	1141 (12)	2413 (10)	133 (14)†	1.8 (2)†
Na(2)	1615 (7)	2612 (6)	-482 (8)	1.3 (1)†
H	-1920	2970	-1520	2.0†

Site populations: Na(1), 0.38(2); Na(2), 0.62.

\* $U_{eq} = \frac{1}{3} \sum_i \sum_j [U_{ij}(a_i^* a_j^*)(a_i, a_j)]$ .

†Isotropic displacement parameter,  $B$ .

Table 2. Coordinates, Co compound

$x, y, z$  and  $U_{eq}^* \times 10^4$ . Space group,  $P\bar{1}$ . Cell dimensions:  $a = 6.535$  (3),  $b = 7.266$  (4),  $c = 6.496$  (3) Å,  $\alpha = 122.96$  (2),  $\beta = 92.28$  (2),  $\gamma = 93.75$  (2)° (GBG).

	$x$	$y$	$z$	$U_{eq}$ or $B$
Co	3544 (1)	1106 (1)	3937 (1)	85 (1)
P(1)	-3796 (2)	3640 (2)	1962 (2)	77 (1)
P(2)	-1427 (2)	2200 (2)	4732 (2)	73 (2)
O(6)	-3273 (4)	537 (5)	4162 (5)	96 (5)
O(2)	-5767 (4)	2480 (5)	1986 (6)	120 (5)
O(5)	347 (4)	1080 (5)	3297 (6)	133 (6)
O(3)	-3854 (5)	5965 (5)	2649 (5)	121 (5)
O(1)	-2900 (5)	2201 (5)	-564 (5)	126 (6)
O(7)	-894 (5)	3729 (5)	7518 (5)	114 (5)
O(4)	-2122 (4)	3794 (5)	3931 (5)	115 (5)
Na(1)	1139 (10)	2437 (8)	171 (12)	1.8 (1)†
Na(2)	1605 (6)	2582 (6)	-470 (8)	1.3 (1)†
H	-1896	2964	-1522	2.0†

Site populations: Na(1), 0.43 (1); Na(2), 0.57.

\* $U_{eq} = \frac{1}{3} \sum_i \sum_j [U_{ij}(a_i^* a_j^*)(a_i, a_j)]$ .

†Isotropic displacement parameter,  $B$ .

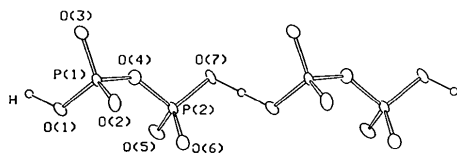


Fig. 1. View of the short (2.44 Å) O(1)···O(7) hydrogen bond between  $HP_2O_7$  groups. The  $c$  axis is horizontal; the view direction is approximately along  $a$ . The atom-numbering scheme has been changed from that used by GBG.

be related to the amount of Zr, for charge balance). The final values of  $P_2$  were 0.93 (2) for the Ni compound and 0.98 (2) for the Co compound; correspondingly, the sums of the two  $Na^+$  site populations were 0.94 (2) and 0.96 (2). There was no appreciable change in either of the  $R$ 's. It is hard to have a lot of confidence in these population parameters (or their sigmas), because they couple strongly with the  $U_{ii}$  values – and, most important, because weights were assigned somewhat arbitrarily (see below). (However,

Table 3. Interatomic distances (Å):  $NaMHP_2O_7$ , space group  $P\bar{1}$ 

	$M = Ni$	$M = Co$
$M-O(1)$	2.165 (4)	2.194 (3)
$M-O(2)$	2.024 (4)	2.042 (3)
$M-O(3)$	2.047 (4)	2.065 (3)
$M-O(5)$	2.072 (4)	2.110 (3)
$M-O(6)$	2.105 (3)	2.138 (3)
$M-O(6)$	2.121 (3)	2.162 (3)
$Na(1)-O(1)$	2.658 (9)	2.641 (7)
$Na(1)-O(2)$	2.283 (9)	2.289 (7)
$Na(1)-O(5)$	2.381 (9)	2.405 (7)
$Na(1)-O(5)$	2.798 (9)	2.750 (7)
$Na(1)-O(6)$	2.890 (9)	2.937 (7)
$Na(1)-O(7)$	2.350 (9)	2.360 (7)
$Na(1)-O(7)$	2.712 (9)	2.712 (7)
$Na(2)-O(1)$	2.950 (6)	2.934 (6)
$Na(2)-O(2)$	2.346 (6)	2.329 (6)
$Na(2)-O(3)$	2.601 (6)	2.620 (6)
$Na(2)-O(5)$	2.478 (6)	2.477 (6)
$Na(2)-O(6)$	2.562 (6)	2.587 (5)
$Na(2)-O(7)$	2.351 (6)	2.392 (6)
$Na(2)-O(7)$	2.490 (6)	2.503 (6)
$Na(1) \cdots Na(2)$	0.583 (9)	0.575 (8)
$P(1)-O(1)$	1.555 (4)	1.555 (3)
$P(1)-O(2)$	1.491 (4)	1.498 (3)
$P(1)-O(3)$	1.498 (4)	1.498 (3)
$P(1)-O(4)$	1.601 (4)	1.601 (3)
$P(2)-O(4)$	1.597 (4)	1.588 (3)
$P(2)-O(5)$	1.504 (4)	1.503 (3)
$P(2)-O(6)$	1.538 (4)	1.530 (3)
$P(2)-O(7)$	1.527 (4)	1.530 (3)
$O(1) \cdots O(7)$	2.442 (5)	2.440 (5)

there was no obviously abnormal pattern to the weighted discrepancies  $\sqrt{w(F_o^2 - F_c^2)}$  in any of the refinements.) There may be small amounts of Zr in the compounds; but it is surely not as much as the  $P_2$  value of 0.5 which would correspond to the composition of the  $P1$  structure proposed by GBG. (GBG report that 'the occupancies of the metals refined to very near unity'. This was not my experience: when I attempted to refine the structure in  $P1$ , starting with the final parameters of GBG, the population of the Zr site dropped to 0.88 and that of the Ni site to 0.93; when the population of the Ni site was fixed at 1.0, that of Zr dropped to 0.85. These refinements showed the typical problems associated with describing a closely centrosymmetric structure in a non-centrosymmetric space group: non-positive-definite  $U_{ij}$  matrices for several atoms and little sign of convergence.)

Interatomic distances and angles (see Table 3) are little changed from the values reported by GBG (but are appreciably more precise). The two sites of the  $Na^+$  ion correspond closely to the positions of Na(1) and Na(2) in the  $P1$  description (after change of origin). The populations of the two sites are unequal in the revised,  $P1$  model, and are closely similar in both compounds; the major site corresponds to Na(2) in the  $P1$  description (GBG) and the minor site to Na(1).

I see no advantage in attempting to refine the structure in space group  $P1$ , and many disadvantages – the many near-singularities associated with describing a closely centrosymmetric structure in a non-centrosymmetric space group (Ermer & Dunitz, 1970; Schomaker & Marsh, 1979). Since the populations of the two Na sites appear to be

appreciably unequal, these sites would also be disordered in  $P1$ . Similarly, the occupancy of at least one of the two ( $M$ , Zr) sites would be disordered if there is any Zr present. (The possibility that one site is entirely  $M$  and the other entirely Zr is ruled out both by the values of the parameter  $P_2$  and by the relatively unsatisfactory results obtained by GBG.) In any event, there is little prospect of detecting any slight deviations from the centrosymmetric  $P\bar{1}$  structure, particularly since GBG followed the usual (and regrettable) procedure of deleting the weakest reflections from their data set (see Marsh, 1981).

Finally, we come to the title question: How much Zr is present in either compound? I believe that the answer is 'Only a small amount'. The small amount would presumably be accompanied by a corresponding deficiency in the occupancy of the  $\text{Na}^+$  sites; according to Goodenough, Hong & Kafalas (1976), such a deficiency would be a prerequisite for  $\text{Na}^+$  mobility. It also seems probable that the amount of Zr can vary from one preparation to another, along with the conductivity of the crystals. I see little chance that the site of the additional proton, H, is other than fully occupied, because of the very short  $\text{O}\cdots\text{O}$  distance. Indeed, this strong  $\text{O}\cdots\text{H}\cdots\text{O}$  bond increases the rigidity of the  $\text{MHP}_2\text{O}_7$  framework (note the small size of

the  $U_{\text{eq}}$  values, Tables 1 and 2), which is another requirement for rapid ion transport (Goodenough *et al.*, 1976). Thus, the correct formula for the compounds is, presumably,  $\text{Na}_{1-2x}\text{M}_{1-x}\text{Zr}_x\text{HP}_2\text{O}_7$ , with  $x$  being 0.1 or less. Note, though, that the results reported here (Tables 1 and 2) were based on a model corresponding to  $x = 0$  – that is, to  $\text{NaMHP}_2\text{O}_7$ .

I greatly appreciate the advice and comments of Dr E. Fowles.

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