# Refinement of the Structure of Sodium Kurrol Salt (NaPO₃)ₓ, Type A

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A full-matrix least-squares refinement using Jost's 1961 data reduced $R(hkl)$ for 760 reflexions to 0·076. The refined bond lengths of the $(PO_3)_\infty$ chain, P–O (bridge) 1·610 and P–O (terminal) 1·479 Å, agree with results for $(RbPO_3)_x$.

The crystal structure of sodium Kurrol salt, type *A*, a polyphosphate of composition $(NaPO_3)_x$, was determined by Jost (1961). The structure was then refined by means of difference syntheses using only $h0l$ and $hk0$ data, although sign determination was carried out by direct methods for the layers $h1l$ to $h5l$ also. The present three-dimensional refinement by least squares uses all the data except the separate $hk0$ reflexions, which are probably more affected by absorption than the others. No absorption corrections were applied. Of a possible 1000 reflexions in the layers $h0l$ to $h5l$ (*ca.* 60% of the Cu sphere), 760 were observed.

$(NaPO_3)_x$, type *A*, crystallizes in the monoclinic space group $P2_1/n$ $(C_{2h}^5)$ and the lattice constants (Jost, 1961) are $a=12\cdot12\pm0\cdot04$, $b=6\cdot20\pm0\cdot02$, $c=6\cdot99\pm 0\cdot03$ Å, $\beta=92\pm0\cdot5°$. In the crystal, helical chains of $PO_4$ tetrahedra run parallel to **b**. The sodium ions have five nearest oxygen neighbours, all of which are terminal atoms.

The starting point of the new refinement, which was carried out (in Glasgow) with the full-matrix least-squares program of Smith and Cruickshank, was the set of atomic coordinates and isotropic vibrational parameters from the earlier refinement. Atomic form factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1962). The weighting scheme used was of the form

$$\sqrt{w}=\{[1-\exp(-P_1(\sin^2\theta)/\lambda^2)]$$
$$\div[1+P_2|F_o|+P_3|F_o|^2+P_4|F_o|^3]\}^{1/2},$$

where the constants took the final values $P_1=500$, $P_2=0\cdot01$, $P_3=0\cdot001$ and $P_4=0\cdot00001$. Initially, atomic coordinates, isotropic vibrational parameters and layer scale factors were refined. After three cycles, the vibrational parameters were allowed to vary anisotropically, with the layer scale factors, but not the overall scale factor, held constant at their converged values. Complete convergence was attained in six more cycles; final $R(hkl)=0\cdot076$ for the 760 observed reflexions. A final difference synthesis showed no peaks over 1 e.Å⁻³. Librational corrections were considered, but are of rather dubious value in an infinite chain structure; however, calculations based on the $P_2O_7$ group and individual $PO_4$ tetrahedra were carried out; the results, which gave corrections of less than a half an e.s.d., were not applied. The final atomic coordinates, vibrational parameters and their e.s.d. are given in Table 1.

Table 1(a). *Final fractional atomic coordinates and e.s.d.**

The asymmetric unit is 2NaPO₃

|  | x/a | y/b | z/c |
|---|---|---|---|
| Na(1) | 0·1310 ± 3 | 0·8688 ± 6 | 0·6287 ± 5 |
| Na(2) | 0·0056 ± 3 | 0·3790 ± 7 | 0·7636 ± 5 |
| P(1) | 0·2154 ± 1 | 0·3624 ± 4 | 0·4914 ± 2 |
| P(2) | 0·1102 ± 1 | 0·1266 ± 4 | 0·1823 ± 2 |
| O(11) | 0·2285 ± 5 | 0·2087 ± 11 | 0·6511 ± 8 |
| O(12) | 0·2169 ± 4 | 0·2370 ± 10 | 0·2884 ± 7 |
| O(13) | 0·1199 ± 4 | 0·5124 ± 11 | 0·4952 ± 8 |
| O(21) | 0·1711 ± 4 | 0·9927 ± 10 | 0·0215 ± 7 |
| O(22) | 0·0416 ± 5 | 0·2942 ± 11 | 0·0865 ± 8 |
| O(23) | 0·0566 ± 5 | 0·9778 ± 11 | 0·3158 ± 8 |

* Refinement e.s.d. × 10⁴.

Table 1(b). *Final vibrational parameters and e.s.d.*

$$f = f_o \exp\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)\right]$$

|        | $U_{11}$      | $U_{22}$      | $U_{33}$      | $2U_{23}$      | $2U_{31}$      | $2U_{12}$      |
|--------|---------------|---------------|---------------|----------------|----------------|----------------|
| Na(1)  | 0·025 ± 2     | 0·020 ± 2     | 0·023 ± 2     | −0·002 ± 3     | −0·005 ± 3     | −0·001 ± 3     |
| Na(2)  | 0·030 ± 2     | 0·019 ± 2     | 0·017 ± 2     | −0·000 ± 3     | 0·003 ± 2      | 0·003 ± 3      |
| P(1)   | 0·013 ± 1     | 0·010 ± 1     | 0·007 ± 1     | 0·001 ± 2      | 0·006 ± 1      | −0·005 ± 2     |
| P(2)   | 0·012 ± 1     | 0·010 ± 1     | 0·008 ± 1     | −0·003 ± 2     | 0·007 ± 1      | 0·000 ± 2      |
| O(11)  | 0·034 ± 3     | 0·022 ± 4     | 0·016 ± 3     | 0·015 ± 5      | 0·004 ± 5      | −0·023 ± 6     |
| O(12)  | 0·018 ± 3     | 0·013 ± 4     | 0·013 ± 2     | −0·008 ± 5     | 0·005 ± 4      | −0·002 ± 5     |
| O(13)  | 0·017 ± 3     | 0·025 ± 4     | 0·020 ± 3     | −0·011 ± 5     | 0·011 ± 4      | 0·004 ± 5      |
| O(21)  | 0·018 ± 3     | 0·014 ± 4     | 0·010 ± 2     | −0·004 ± 4     | 0·004 ± 4      | 0·001 ± 5      |
| O(22)  | 0·022 ± 3     | 0·023 ± 4     | 0·018 ± 3     | 0·002 ± 5      | −0·007 ± 4     | 0·018 ± 5      |
| O(23)  | 0·022 ± 3     | 0·022 ± 4     | 0·014 ± 3     | 0·004 ± 5      | 0·019 ± 4      | −0·012 ± 5     |

* Refinement e.s.d. × 10$^3$. Vibrational parameters along **b** will be subject to additional errors owing to their correlation with layer scale factors in the absence of *hk0* data from the refinement.

Table 2. *Interatomic distances and e.s.d.* (Å)

| P–O (peripheral) |           | P–O (bridging)  |           |
|------------------|-----------|-----------------|-----------|
| P(1)–O(11)       | 1·472 ± 7 | P(1)–O(12)      | 1·619 ± 6 |
| P(1)–O(13)       | 1·486 ± 6 | P(1)–O(21′)     | 1·600 ± 6 |
| P(2)–O(22)       | 1·477 ± 7 | P(2)–O(12)      | 1·620 ± 6 |
| P(2)–O(23)       | 1·479 ± 6 | P(2)–O(21)      | 1·599 ± 6 |
| Mean             | 1·479     | Mean            | 1·610     |

| Na(1) polyhedron |           | Na(2) polyhedron |           |
|------------------|-----------|------------------|-----------|
| Na(1)···O(13)    | 2·401 ± 7 | Na(2)···O(22″)   | 2·343 ± 7 |
| Na(1)···O(11)    | 2·419 ± 7 | Na(2)···O(22′)   | 2·360 ± 7 |
| Na(1)···O(23)    | 2·432 ± 7 | Na(2)···O(23′)   | 2·396 ± 7 |
| Na(1)···O(11′)   | 2·464 ± 7 | Na(2)···O(13′)   | 2·419 ± 7 |
| Na(1)···O(23′)   | 2·506 ± 7 | Na(2)···O(13)    | 2·511 ± 6 |
| Mean             | 2·444     | Mean             | 2·406     |

| | |
|---|---|
| Na(1)···O(21) | 2·876 ± 7 |

* From refinement e.s.d. only (× 10$^3$). All distances are subject to an additional uncertainty of ca. 0·4% because of the large e.s.d. in cell dimensions. Thus a truer e.s.d. for P–O distances is 0·010 Å.

Table 3. *Angles and e.s.d.*

Bridging oxygen atoms:

| | | |
|---|---|---|
| P(1)–O(12)–P(2)  | 124·8 ± 0·3° | |
| P(2)–O(21)–P(1′) | 136·1 ± 0·4  | |

PO$_4$ tetrahedra:

| O(11)–P(1)–O(12)  | 110·5 ± 0·4° | O(12)–P(2)–O(21) | 99·2 ± 0·3°  |
|-------------------|--------------|------------------|--------------|
| O(11)–P(1)–O(13)  | 117·1 ± 0·3  | O(12)–P(2)–O(22) | 109·8 ± 0·4  |
| O(11)–P(1)–O(21′) | 107·4 ± 0·4  | O(12)–P(2)–O(23) | 109·7 ± 0·3  |
| O(12)–P(1)–O(13)  | 110·4 ± 0·3  | O(21)–P(2)–O(22) | 108·3 ± 0·3  |
| O(12)–P(1)–O(21′) | 99·1 ± 0·3   | O(21)–P(2)–O(23) | 110·1 ± 0·3  |
| O(13)–P(1)–O(21′) | 110·9 ± 0·3  | O(22)–P(2)–O(23) | 118·2 ± 0·3  |
| Mean              | 109·2        | Mean             | 109·2        |

* From refinement e.s.d. only.

The numbering of the atoms follows the paper of Jost (1961). Tables 2 and 3 give bond lengths and angles. Tables of observed and calculated structure factors can be obtained from one of us (K.H.J.) upon request.

All the crystallographically different P–O(bridge) and P–O(terminal) bond lengths are within about 0·01 Å of their respective mean values, 1·610 and 1·479 Å. They are very similar to the bond lengths 1·616 and 1·488 Å in (RbPO$_3$)$_x$ (Corbridge, 1956; Cruickshank, 1964). The lengths of the individual P–O(bridge) bonds do not alternate (short–long–short, etc.), in contrast to the earlier supposition of Jost (1961). The sodium ion Na(1) has a sixth oxygen atom neighbour, bridging atom O(21), which is about 0·4 Å further away than the five terminal atoms mentioned before.

**References**

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