

X-Ray Investigation of Potassium *p*-Nitrosophenolate Monohydrate

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The present structure investigation of potassium *p*-nitrosophenolate monohydrate is part of a series of structural investigations of *para* substituted nitrosobenzenes and oximes derived from these by protonation or tautomeric proton exchange. Lüttke¹ has demonstrated the ability of *para* substituted nitrosobenzenes in forming dimers of the azodioxy-type to be heavily dependent upon the electron donating ability of the *para* substituent. An intramolecular charge transfer from the *para* substituent to the nitroso group is probably preventing dimerisation. A comparison of the molecular structure of these nitrosobenzenes and their corresponding oximes should indicate to what degree this intramolecular charge transfer is present.

So far the crystal and molecular structure of *N,N*-dimethyl-*p*-nitrosoaniline,² its hydrochloride,³ and quinone-4-oxime⁴ have been investigated.

Potassium *p*-nitrosophenolate monohydrate was formed in ethanolic solutions of *p*-nitrosophenol and potassium hydroxide. Recrystallisation from pure acetone gave suitable tabular green crystals. The crystal data are as follows: Potassium *p*-nitrosophenolate monohydrate, $\text{KC}_6\text{H}_5\text{O}_2\text{N}\cdot\text{H}_2\text{O}$, orthorhombic, space group $P2_12_12_1$. Cell dimensions: $a = 5.527(4)$ Å, $b = 7.558(4)$ Å, $c = 18.883(13)$ Å, $V = 788.9$ Å³, $M = 179.22$, $F(000) = 364$, $Z = 4$, $\mu = 0.621$ mm⁻¹, $D_{\text{obs}} = 1.52$ g cm⁻³, $D_{\text{calc}} = 1.51$ g cm⁻³.

The intensity data were collected using an automatic Picker diffractometer with graphite crystal monochromated $\text{MoK}\alpha$ radiation. The crystal used was $0.40 \times 0.40 \times 0.12$ mm³. 404 reflections with $I \geq 2\sigma(I)$ (1300 reflections with $2\theta \leq 60^\circ$ were measured) were regarded as observed. The intensity data were corrected for absorption effects.

Disregarding 18 small reflections the data are consistent with the space group $\text{Pan}2_1$. Fourier refinement of the potassium atom coordinates in this space group revealed all other non-hydrogen atoms but subsequent least squares refinement did not converge ($R = 32\%$). Using the space group $P2_12_12_1$ least squares refinements terminated with $R = 9.7\%$. Only the potassium and the water oxygen atom were refined anisotropically. Refinement with anisotropic thermal parameters for all non-hydrogen atoms gave unreasonable results. The goodness of fit was approximately 3. The result of the structure analysis is given in Fig. 1. The estimated standard deviations are 0.03 Å in the bond lengths and 2° in the angles.

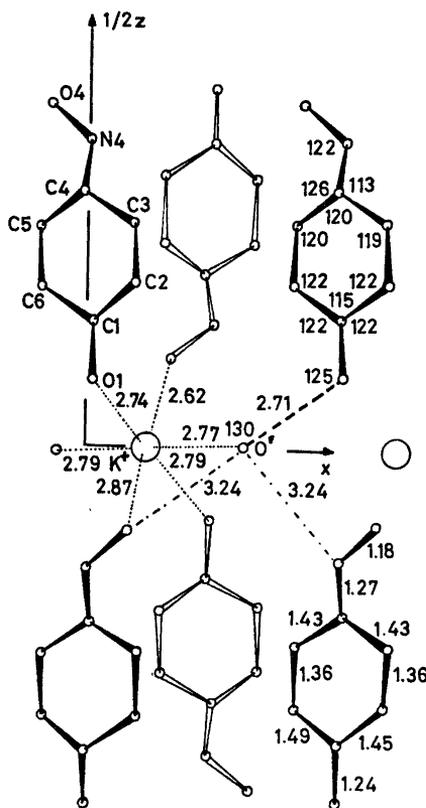


Fig. 1. The potassium salt of *p*-nitrosophenolate. Bond lengths (Å) and angles ($^\circ$), $R = 9.7\%$ (the atoms in the anion moiety are refined isotropically). The $\text{O1}\cdots\text{HO}'$ hydrogen bond is indicated by broken line, the coordination about the potassium atom by dotted lines and the two shortest contacts to O' by the $-\cdot-\cdot-$ lines.

The anion is almost planar, and apart from the NO bond length being shorter and the CNO angle larger than expected, the bond lengths and angles are rather similar to the corresponding bond lengths and angles found in quinone-4-oxime.⁴ Thus the quinonoid character of the anion seems to be pronounced indicating a strong intramolecular charge transfer.

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