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Adventitious Isolation and Crystal Structure of Potassium 2,4-Dinitrophenolate

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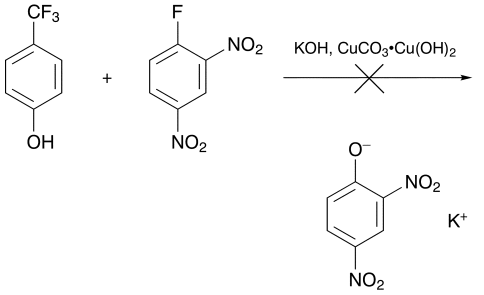
Potassium 2,4-dinitrophenolate was isolated from an attempted Ullman coupling reaction, and its crystal structure determined.

In an attempt to prepare a range of substituted diaryl ethers for structure activity studies, we attempted the Ullman coupling[1] of 4-trifluoromethylphenol with 2,4-dinitrofluorobenzene. Unfortunately the 4-trifluoromethylphenol proved to be unstable to the strongly basic conditions, and potassium 2,4-dinitrophenolate **1** was isolated, having been formed by KOH hydrolysis of the 2,4-dinitrofluorobenzene.



1

The structure of **1** was determined by X-ray crystallography (Fig. 1). K(1) is seven-coordinate, being bound to two chelating *para*-nitro groups, two phenoxide oxygen atoms and the water molecule. Although the *para*-nitro groups are technically chelating, the chelate is distinctly non-symmetric with K(1)—O(1) = 2.809(4) and K(1)—O(2) = 3.118(3) Å. K(2) is ten-coordinate being bound to two chelating *ortho*-nitro groups, two phenoxy/*ortho*-nitro chelating molecules and two monodentate *para*-nitro groups. The *para*-nitro groups are relatively weak donors [K(2)—O(2) = 3.103(4) Å] and the *ortho*-nitro chelates are highly non-symmetric [K(2)—O(3) = 3.181(3), K(2)—O(4) = 2.961(4) Å]. The OH of the water molecule is hydrogen-bonded to the phenoxide oxygen and the bond lengths in the aromatic ring show substantial quinonoid distortion.[10] The structure is best compared with alkali metal *para*-nitrophenolates and picrates. The structures of the calcium and magnesium derivatives of 2,4-dinitrophenol are the only salts of this phenol that have been structurally characterised, but in these cases metal coordination is dominated by water.[2]

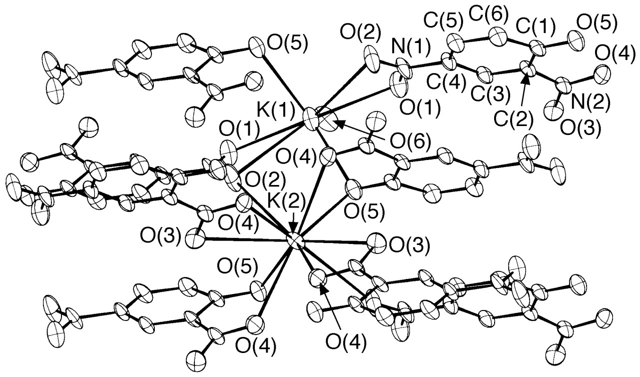


Fig. 1 Structure of **1**. *Crystal data for* $C_6H_4KN_2O_{5.5}$. $M = 231.2$, monoclinic, $C2/c$, $a = 20.713(2)$, $b = 12.288(1)$, $c = 7.181(1)$ Å, $\beta = 109.58(1)^\circ$, $Z = 4$. The structure was solved by direct methods using SHELXS-86 with non-H atoms anisotropic, H atoms isotropic. $R = 0.05$, $R' = 0.058$, 1151 reflections used in refinement. The K cations and water molecule lie on a crystallographic two-fold rotation axis. C(1)—C(2) 1.441(6), C(2)—C(3), 1.372(6), C(3)—C(4) 1.361(7), C(4)—C(5) 1.401(7), C(5)—C(6) 1.341(7), C(6)—C(1) 1.438(6) Å

Techniques used: X-Ray crystallography

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References cited in this synopsis

1 J. Lindley, *Tetrahedron*, 1984, **40**, 1433.
2 L. B. Cole and E. M. Holt, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1997.
10 D. J. Hughes, *J. Chem. Soc., Dalton Trans.*, 1973, 2347.

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