Synthesis and Crystal Structure of a Nonionic Compound of Sodium, (1-Phenylbutane-1,3-dionato)(ethylene glycol)sodium

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Summary A compound of sodium, which gives non-conducting solutions in organic solvents has been synthesized and its crystal structure determined.

In their pioneer work on alkali-metal complexes, Brewer and Sidgwick[1] contrasted the β-diketonate 'salts' insoluble in toluene with 'complexes' which were soluble in that solvent. One such complex was the dihydrate of sodium benzoylacetonate (or 1-phenylbutane-1,3-dionate referred to as BZAC below).

We repeated the synthesis and confirmed the composition by *X*-rays, but the tendency for tri- and tetra-hydrates to be formed with equal ease and for the water of hydration to be lost on heating suggested that some or all might be lattice rather than co-ordinated water. By recrystallising NaBZAC from ethanol containing 4% glycol we obtained the compound $Na(PhCO{\cdot}CH{\cdot}CO{\cdot}CH_3)HOCH_2{\cdot}CH_2OH$ which can be dissolved in and recrystallised from hot toluene. It dissolves in several other solvents, *N*-methylpyrrolidone, nitromethane, and acetone, in which it has zero electrical conductivity. The compound melts, with decomposition, at 135—137°. The molecular weight determined osmometrically in acetone is concentration dependent, 228 at 0·006 M and 310 at 0·061 M. Determination of relative numbers of hydrogen atoms by ^{1}H n.m.r. confirmed the empirical formula but no structurally diagnostic results were obtained. In the i.r. spectrum the bands usually found[2] for a chelated β-diketone were obtained as were two for the OH of glycol, 3305 and 3260 cm^{-1}; the splitting and downward shift from the band at 3330 cm^{-1} in glycol itself[3] indicate that the molecule is co-ordinated. It is not, however, chelated but bridging as shown by crystal structure analysis.

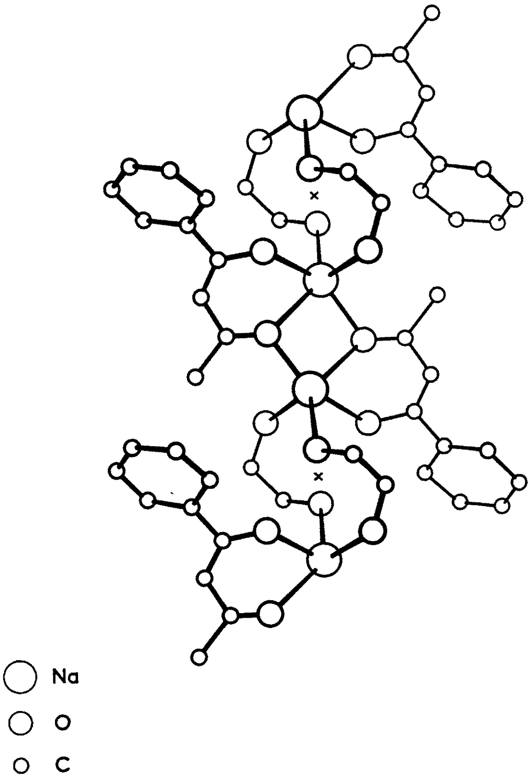

Figure. *Part of the structure projected along the* [01$\bar{1}$] *axis. The upper cross represents the centre of symmetry at* 0,0,0, *the lower that at* 0,1,1 *of one unit cell. From left to right the chain lies within the limits* +a/2 *to* −a/2.

Crystal data: $C_{12}H_{15}O_4Na$. $M = 246$. Triclinic, $a = 12{\cdot}24$, $b = 7{\cdot}62$, $c = 7{\cdot}28$ Å, $\alpha = 112{\cdot}5°$, $\beta = 83{\cdot}0°$, $\gamma = 86{\cdot}7°$, $U = 618{\cdot}8$, $D_m = 1{\cdot}30$, $Z = 2$, $D_c = 1{\cdot}32$. Cu-K_α radiation, [λ for Cu-$K_{\alpha 1} = 1{\cdot}54051$ Å (10^{-10}m)].

Intensities were estimated visually on Weissenberg photographs taken at room temperature. The structure was solved by direct methods and refined by least-squares to the present R of 0·16 for 1256 reflections. A view along $[01\bar{1}]$ is shown in the Figure; the structure consists of centrosymmetric dimeric molecules, formed by two glycol molecules acting as bridges between the two sodium atoms. Each sodium is five-co-ordinated by oxygen atoms from two glycol molecules, by two oxygen atoms from a chelate β-diketone molecule, and by one oxygen from another β-diketone. In the crystal the dimeric molecules are held by bridging oxygen atoms giving centrosymmetrical Na–O–Na–O rings. All Na–O distances lie in the range 2·2—2·3 Å. The chains are held by van der Waals' forces between the phenyl groups, and this weak bonding accounts for the marked cleavage of the crystals, parallel to (100).

On dissolution the chains may break to give dimeric molecules initially but the concentration-dependent molecular weight indicates the presence of more than one (possibly solvated) species.

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