18-Crown-6–Potassium–Ethyl Acetoacetate Enolate. *X*-Ray Structure Determination

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Summary The crystal structure of the title compound shows that it forms a distinct molecule; K^+ is co-ordinated to the six oxygen atoms of the crown and to the two oxygen atoms of the U shaped enolate.

THE reactivity of anionic nucleophilic enolates mainly depends upon the cation and the complexing agents added (crown ethers[1] and cryptands[2]). A general study of β-dicarbonyl enolate anions has been undertaken in order to correlate their reactivity with the structural features which were proposed for these anions. ^{23}Na N.m.r. and i.r. spectroscopy,[3] and *X*-ray diffraction analysis are being used together to identify the different species (U, S, or W shape[4]) present in solution, i.r. spectroscopy allowing correlation from solid state to solution.[5] Arnett and DePalma[6] have just published an investigation of ion-pairs in solution by different methods. Although their assignment of the far-i.r. spectrum of their solutions in THF (tetrahydrofuran) might be questioned, they were able to demonstrate that certain bands are caused by the presence of ion pairs with strong cation–anion interactions.

Various complexes with different cations and crowns are under investigation and we report here the crystal structure of the 18-crown-6–potassium–ethyl acetoacetate enolate which provides the first example of a 'crowned' alkali metal enolate ion-pair.[7]

Twinned crystals were grown from a 1 : 1 solution (0·2 M) of K^+ ethyl acetoacetate and 18-crown-6 in THF by slow cooling. Some of these crystals could be cleaved into nontwinned fragments which were sealed in a thin-walled capillary.

Crystal data: $C_{12}H_{24}O_6,C_6H_9O_3^-K^+$; $M = 438$; monoclinic; space group $P2_1/n$; $a = 9{\cdot}110(5)$, $b = 18{\cdot}596(14)$, $c = 14{\cdot}315(12)$ Å, $\beta = 108{\cdot}02(8)$; $Z = 4$; $D_c = 1{\cdot}26$ g cm^{-3}. Single-crystal *X*-ray diffraction data were measured with a Philips PW 1100 diffractometer using the ω–2θ scan technique with graphite-monochromated Cu-K_α radiation ($\lambda = 1{\cdot}54178$ Å). The intensities of three standard reflexions decreased with time in an isotropic manner and a correction was applied during data processing. This was probably due to a slight amount of moisture in the capillary. The structure was solved by conventional direct methods.[8] Full-matrix least-squares refinement, including all hydrogen

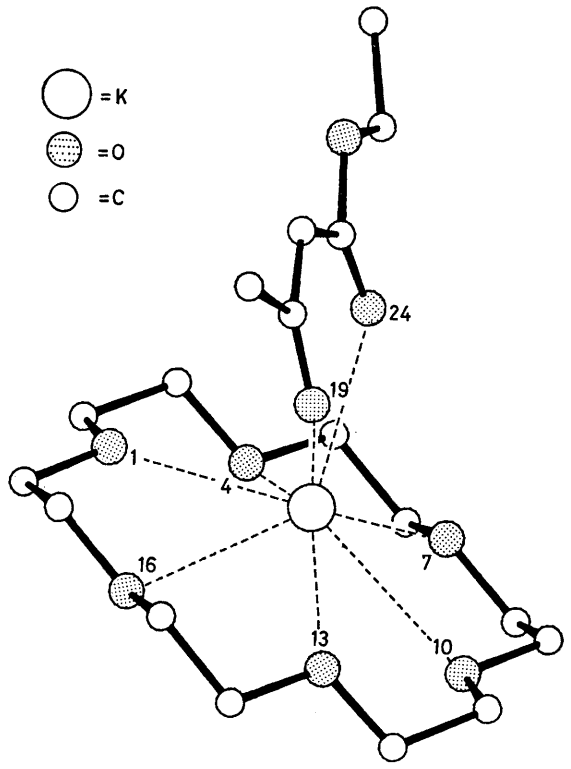

FIGURE. Structure of 18-crown-6–potassium–ethyl acetoacetate enolate. K–O(1) 2·827, K–O(4) 2·972, K–O(7) 2·922, K–O(10) 2·931, K–O(13) 2·903, K–O(16) 3·015, K–O(19) 2·651, K–O(24) 2·733 Å.

atoms, with anisotropic temperature factors for the non-hydrogen atoms resulted in an *R*-factor of 0·065, based on 2157 observed reflexions.†

The 'crowned' ion-pair forms a distinct molecule (Figure). The cation is co-ordinated to eight oxygen atoms, and the enolate is quite planar, having a slightly opened U shape. The conformation of the crown is quite similar to that observed in the complexes with KNCS, RbNCS, and CsNCS.[9] The six oxygen atoms lie alternately 0·25 Å above and below the mean plane of the crown. The K^+ atom is displaced by 0·9 Å out of this plane towards the strongly chelating [4a] anion of ethyl acetoacetate. It is interesting that in the crown complex with the monodentate anion SCN^- the cation is situated exactly in the mean plane of the crown.[9] The plane of the enolate makes an angle of 52° with the mean plane of the crown, K^+ being out of this plane by 0·9 Å.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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