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CRYSTAL DATA FOR TWO COMPLEXES OF ETHYL PICRATE WITH ALKALI ETHYLATES

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In recent literature, there has been a considerable interest in complexes of alkyl picrates with potassium ethylate or methylate (Meisenheimer salts). The infrared spectra of a series of these substances have been published by Foster and Hammick (1) and, in a more complete form, by Dyall (2). For some of these compounds, the absorption spectra in the visible have been reported by Foster (3). A nuclear magnetic resonance study has been made by Crampton and Gold(4).

The electronic and molecular structure of the Meisenheimer salts is of particular interest to us, as these compounds are strictly related to transition states or intermediates in aromatic nucleophilic substitution reactions (5, 6, 7).

As a first step in determining the crystal structures of the Meisenheimer salts, crystallographic data for the complexes of potassium and cesium ethylates with ethyl picrate have been obtained (Table 1).

The Cs salt was prepared along the lines of the procedures followed by Farmer (8) and Dyall (2) for the K salt, except that Cs ethylate was prepared by Thomas's (9) method. Crystals of the Cs salt were obtained from ethanolic solution as red needles, elongated along b. The crystals decompose rapidly

above 200°C.

The identity of the products was checked by a partial chemical analysis (see Table 2) and infrared spectra. In Figure 1, where these spectra are shown, the close similarity between the two substances is particularly evident.

The cell constants, except b of the Cs salt, were obtained by Cohen's back reflection method, as described by Buerger (10). The effective radius of the camera (an ordinary Weissenberg) was determined by mounting the film according to Straumanis technique.

The standard deviations, shown in Table 1 are derived from the sum of the residuals, according to Whittaker and Robinson (11). Though in the case of the potassium salt suspiciously too low, they agree very well with the differences between the values observed from different crystals, measured in different cameras.

The space group for the potassium salt is assumed to be $P\bar{1}$, because of absence of piezoelectricity (although the morphology of some crystals would suggest P 1) : in the case of the Cs compound, the observed extinctions lead uniquely to $P\,2_1/c$. Since no crystal mounted on a h 0 l axis was available, the (0k0) extinctions (k odd) were observed in a precession photograph.

The similarity between the cell constants of the two substances reflects the similarity expected from chemical considerations.

TABLE 1

Unit cell parameters (at 20°C)

	$KC_{10}H_{12}N_3O_8$	$CsC_{10}H_{12}N_3O_8$
a	14.7443 ± 0.0008 Å	15.564 ± 0.003 Å
b	10.2848 ± 0.0004 Å	10.54 ± 0.02 Å
c	9.9919 ± 0.0004 Å	19.919 ± 0.001 Å
α	105.901 ± 0.006°	-
β	104.05 ± 0.01°	110.31 ± 0.01°
γ	97.15 ± 0.01°	-
System	triclinic	monoclinic
Space gr.	$P\bar{1}$	$P2_1/c$
Z	4	8
Cell volume	1383.6 $Å^3$	3064.4 $Å^3$
D_{calc}	1.638 g/cm^3	1.890 g/cm^3
D_{meas}	1.640 g/cm^3	1.878 g/cm^3

TABLE 2

Results of chemical analysis

	Cs	C	H	N	O	K
Calculated for $CsC_{10}H_{12}N_3O_8$:	30.54	27.60	2.78	9.66	29.42	-
Found (per cent):		27.10	2.80	9.68		
Calculated for $KC_{10}H_{12}N_3O_8$:	-	35.19	3.54	12.31	37.50	11.46
Found (per cent):		35.42	3.32	12.44		

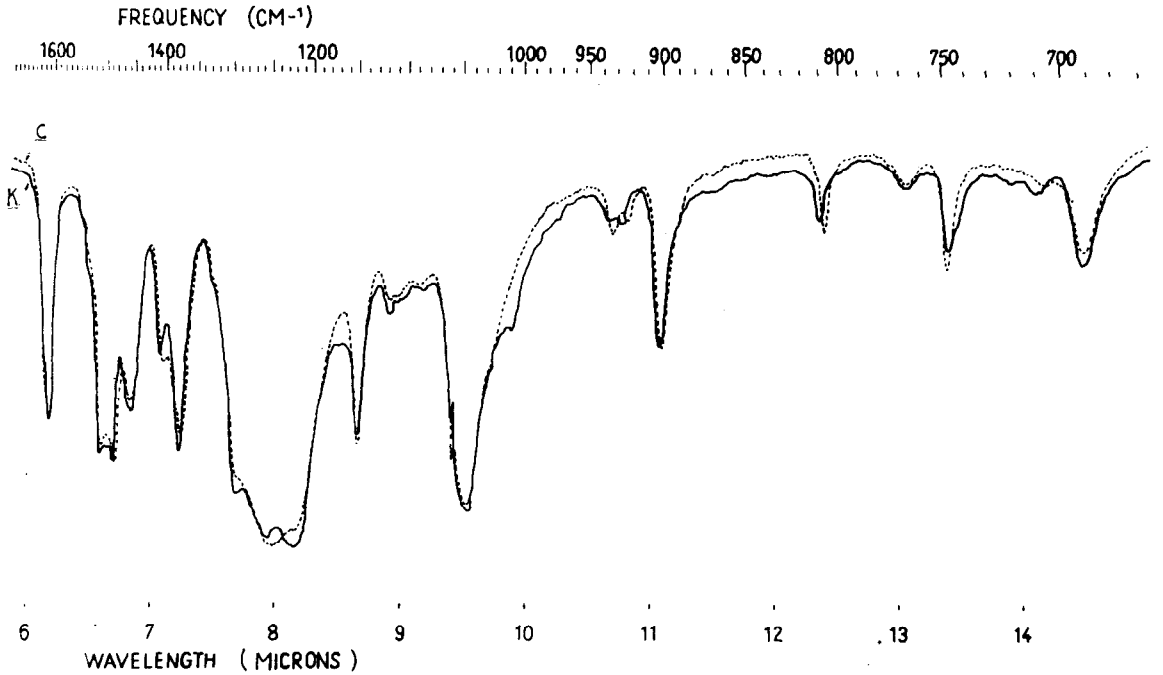

Fig.1 Infrared spectrum of the complex of ethyl picrate with cesium ethylate. The spectrum of the corresponding potassium compound is superimposed.

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