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X-ray diffraction data for methyl- and ethyl-lithium.

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Introduction

This note reports the results of an X-ray diffraction investigation of crystalline methyl- and ethyl-lithium. These compounds are of particular interest in connection with the theory of electron-deficient bonding (Coates, 1950); there has, however, been no work reported on the structures of these two compounds.

The methods of preparation are described elsewhere (Brown & Rogers, 1957); it was possible to obtain large, well formed crystals of ethyl-lithium, but not of methyl-lithium. The latter is an insoluble microcrystalline precipitate as prepared, and no solvent was found from which crystals could be grown. All operations involving the crystalline materials were carried out in a dry box, since the compounds are extremely reactive with air and water; however, it was possible to mount both single crystals and powder samples in thin-walled glass capillaries for the X-ray work. Both single-crystal and powder photographs were obtained for ethyl-lithium, but powder photographs only for the methyl compound. A Norelco Model 5001 diffraction machine equipped with copper-target tube (and Ni filter) operated at 35 kV. and 20 mA. was employed, along with standard rotation and powder cameras.

Ethyl-lithium

Microscopic observations of the ethyl-lithium crystals under crossed Nicols revealed that the crystals were optically active when viewed along one of the crystal axes. Although the specific rotation was not measured, it appeared to be large ($> 10°$ mm.$^{-1}$). Single-crystal rotation photographs were in agreement with orthorhombic symmetry for the crystals and all of the thirty-one observed lines in the powder diagrams could be indexed on this basis. The only systematic absences observed were the $00l$ reflections with l odd. Since the crystals are optically active the enantiomorphous space group $P222_1$ appears to be the correct assignment. Rough values of the unit-cell dimensions were determined from the rotation photographs and the more precise values

$$a_0 = 6{\cdot}65,\ b_0 = 9{\cdot}03,\ c_0 = 8{\cdot}10 \text{ Å}$$

were obtained from the powdered diffraction data. The probable error in these values is perhaps $\pm 0{\cdot}05$ Å. If the number of molecules per unit cell is assumed to be eight, a density for the solid of 0·98 g.cm.$^{-3}$ is obtained. Although the density of the crystals was not measured it was greater than that of benzene (0·87 g.cm.$^{-3}$). The quality of the single-crystal photographs obtained was not good enough to permit satisfactory estimates of intensity, nor did they extend to large enough values of scattering angle. Efforts are underway to obtain photographs suitable for a detailed structural analysis.

Methyl-lithium

Microscopic observation of methyl-lithium crystals revealed that they are isotropic in all orientations and it was possible to index the powder photographs on the basis of cubic symmetry. Although exposures of up to 24 hr. were made, only about 20 lines were observed. These are listed in Table 1 along with the values of d_{hkl}. Values of a_0 and of the visually estimated intensities of the lines are also given.

Table 1. *Data from powder photographs of methyl-lithium*

Line	d (Å)	a_0 (Å)	Intensity	hkl
1	8·83	8·83	4	100
2	6·29	8·89	9	110
3	5·127	8·88	3	111
4	3·956	8·846	3	210
5	3·135	8·853	1–2	211
6	3·000	8·866	2	220
7	2·8167	9·000	10	300, 221
8	2·5638	8·907	2	310
9	2·4656	8·881	1	222
10	2·3756	8·890	2	320
11	2·1610	8·888	1	321
12	2·0980	8·905	1	410
13	1·9505	8·901	1–2	411, 330
14	1·9000	8·951	1–2	331
15	1·8658	8·938	1	421
16	1·7802	8·912	1–2	332
17	1·7466	8·906	1–2	442
18	1·7150	8·901	1	500, 430
19	1·6587	8·906	1	510, 431
20	1·7150	8·911	1–2	511, 333
21	1·6587	8·932	1–2	520, 432
22	1·5522	8·917	1	522, 441

An average value of the unit cell dimension, $a_0 = 8{\cdot}909 \pm 0{\cdot}016$ Å, was obtained from these data. The crystals were observed to have about the same density as a solution consisting of about 80% benzene (density 0·89 g.cm.$^{-3}$) and 20% pentane (density 0·63 g.cm.$^{-3}$). If it is assumed that there are 16 molecules per unit cell, a density for the solid of 0·826 g.cm.$^{-3}$ is calculated. Since the reflections show no systematic absences the lattice must be primitive but there remains a choice of five possible space groups; our data were not adequate to choose among these.

References

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