

The form of $p(\eta, T)$ obtained in the previous section [Eq. (10)] is verified by the plots in Figs. 3(a)–3(c). The validity of Eq. (5) for τ_{enc} is assumed. The simple unimolecular reaction model is thus seen to account in a satisfactory way for the exchange probability parameter $p(\eta, T)$. Interestingly enough, it is empirically found that $J_0\tau_{\text{enc}}$ for radical–radical exchange is strongly solvent-dependent, and that for the same solvent (methyl cyclohexane) $J_0\tau_{\text{enc}} \gg J_0'\tau'_{\text{enc}}$. The values of $J_0\tau_{\text{enc}}$ are found to be $1.01 \times 10^3 \eta/T$ (*n*-pentane), $2.81 \times 10^3 \eta/T$ (propane), $\approx 1 \times 10^3 \eta/T$ (methylcyclohexane), while $J_0'\tau'_{\text{enc}} = 0.19 \times 10^3 \eta/T$ (methylcyclohexane). Viscosities are expressed in centipoise.

From the empirical values of $J_0\tau_{\text{enc}}$ and Eq. (5) with $\lambda = 3 \times 10^{-8}$ cm, J_0 was calculated to be 1.6×10^{11} sec⁻¹ in *n*-pentane, 4.5×10^{11} sec⁻¹ in propane and $\approx 1.6 \times 10^{11}$ sec⁻¹ in methylcyclohexane. $J_0'\tau'_{\text{enc}}$ is

about an order of magnitude smaller than the corresponding quantity for radical–radical exchange. It is expected, however, that λ' , the interaction radius for the oxygen molecule, is also appreciably smaller. These values of J_0 are about an order of magnitude larger than the value estimated by Pake and Tuttle² for polycrystalline DPPH (10^{10} – 10^{11} sec⁻¹).

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Crystal Structure of $\text{Li}_6\text{BeF}_4\text{ZrF}_8$ †

D. RICHARD SEARS AND JOHN H. BURNS

Reactor Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

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The crystal structure of $\text{Li}_6\text{BeF}_4\text{ZrF}_8$ has been determined by x-ray diffraction. The tetragonal unit cell, having $a = 6.57$, $c = 18.62$ Å, contains four formula weights; the space group is $D_{4h}^{19} - I4_1amd$. Discrete BeF_4^{2-} and ZrF_8^{4-} ions are connected by shared Li^+ ions. The BeF_4^{2-} tetrahedron is quite regular with a Be–F distance of 1.57 ± 0.01 Å; the ZrF_8^{4-} dodecahedron has two independent Zr–F bonds of 2.05 ± 0.01 Å and 2.16 ± 0.01 Å, and deviates considerably from the shape predicted by theory.

INTRODUCTION

ZIRCONIUM is known to occur as the central atom of a variety of complex coordination polyhedra, often bearing eight ligands arranged in dodecahedral or square-antiprismatic symmetry.^{1,2} Racah³ and Duffey⁴ have derived orbital strengths for these configurations using $d^4s^2p^3$ hybridization. Their calculations established no significant energy difference between the configurations, if isolated complexes are considered.

The configuration adopted in a particular crystal is therefore determined in part by external influences, such as ligand–ligand repulsions, constraints due to

bonding between ligands, and packing requirements. Thus it is interesting to examine MX_8 -type configurations in which, as in the well known $\text{Mo}(\text{CN})_8^{4-}$ ion,⁵ the central metal atom is bonded to eight apparently equivalent monodentate ligands.

In an investigation of the phase diagram of the ternary system $\text{LiF} - \text{BeF}_2 - \text{ZrF}_4$, Thoma *et al.*⁶ discovered a primary phase of composition $6\text{LiF} \cdot \text{BeF}_2 \cdot \text{ZrF}_4$. The stoichiometry and preliminary x-ray studies suggested the possible occurrence of complex octafluorozirconate and tetrafluoroberyllate ions in the crystal.

The coexistence of two discrete complex anions in a crystal is not common. But since it seemed likely in this compound, a crystal-structure analysis was carried out to examine in detail the configuration of the discrete

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³ G. Racah, *J. Chem. Phys.* **11**, 214 (1943).

⁴ G. H. Duffey, *J. Chem. Phys.* **18**, 746, 1444 (1950).

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⁶ R. E. Thoma *et al.*, U.S. Atomic Energy Commission Report ORNL-3591 (1964), pp. 3 ff.

ZrF_8^{4-} ion and bond distances

A single crystal melt of stoichiometric $\text{Li}_6\text{BeF}_4\text{ZrF}_8$ at 471°C. Neutron diffraction analyses indicate the ZrF_8^{4-} ion and this $\text{Li}^+/\text{Zr}^{4+}$ ratio.

X-ray precession method yielded a tetragonal unit cell with $a = 0.02$, $c = 18.62$ Å, space group $I4_1/amd$. An electron density map was obtained by a Fourier method. However, an electron density map of the compound was obtained by the method of volumes of the unit cell from which the density is 3.06 g cm^{-3} .

Photograph of the hkl reflections from radiation and spot densities by visual comparison with strips. Of the comparison with the range of the values.

The $\text{CuK}\alpha_1$ radiation is 139 cm^{-1} . The 0.01 cm parallel to that in the errors were estimated for them was applied to the relative structural scale was four

STRUCTURE

The beryllium symmetry to Group $I4_1/amd$ not wholly in the method, together with atomic contributions to the structure from electron

⁷ A. J. C. Wilkins

⁸ International Union of Pure and Applied Chemistry, Birmingham

⁹ All Fourier

were done with

FORDAP-2 with

and R. D. Ellis