at an initial pressure of about 250 mm. White, well-defined crystals of $P_4O_6 \cdot B_2H_6$ formed slowly. Fractionation of volatiles gave unreacted P_4O_6 and/or B_2H_6 but no other materials. In eight runs the initial ratio of B_2H_6/P_4O_6 was varied from 0.35 to 5.0, but the ratio of B_2H_6 *reacting* with P_4O_6 was 1.00 ± 0.03. The X-ray powder pattern using Fe Kα radiation was recorded with a camera 114.6 mm in diameter. The *d* values (uncorrected for film shrinkage) are given in Angstrom units: 8.8 (m), 8.2 (m), 7.1 (vs), 6.55 (vw), 6.19 (w), 5.34 (m, diffuse), 4.79 (s), 4.36 (w), 3.94 (w), 3.65 (m), 3.37 (w), 3.11 (m), 2.94 (w), 2.81 (vw), 2.70 (vw), 2.59 (vw), 2.50 (vw), 2.426 (vw), 2.362 (w). The compound is very hygroscopic and hydrolyzes readily, usually catching fire when brought in contact with a drop of water.

The ^1H nmr spectrum of a methylene chloride solution of the compound was obtained at 29°. Four equally spaced broad peaks due to three protons attached to boron were observed. The value of J_{B-H} of 100 cps is clearly inconsistent with a BH_4^- ion (78 cps),[4a] but is close to the values for BH_3 groups bound to phosphorus ligands.[4b] Our observation that treatment of the methylene chloride solution of the compound with anhydrous HCl did not yield B_2H_6 and H_2 gas also confirms the absence of BH_4^- in the compound.

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Received January 24, 1966

Isomorphous Complex Fluorides of Tri-, Tetra-, and Pentavalent Uranium[1]

Sir:

We wish to report the first preparation of complex fluorides formed between UF_3 and the alkali fluorides KF, RbF, and CsF. The $3KF \cdot UF_3$ crystalline phases are of face-centered cubic symmetry and isomorphous with the $3KF \cdot UF_4$ and $3KF \cdot UF_5$ analogs with nearly identical cell parameters. The significance of this finding is that the oxidation state of uranium in some cases can be varied for oxidation numbers III to V (and perhaps VI) within pure single-phase, crystalline compounds without affecting the crystal symmetry.

Recently many new compounds were found to be formed between the alkali fluorides and the fluorides of pentavalent actinides, protactinium,[2–5] uranium,[6–8] neptunium,[9] and plutonium.[10] The crystalline compounds formed between alkali fluorides and UF_4 have also been studied extensively.[11,12] However, except for $NaF \cdot UF_3$,[13a] no compounds between UF_3 and alkali fluoride were known.

Ruedorff and Leutner[6] reported that the X-ray powder diffraction photographs of $3NaF \cdot UF_4$ and $3NaF \cdot UF_5$ were almost identical and that the unit cell of $3NaF \cdot UF_5$ is but slightly larger than $3NaF \cdot UF_4$. On comparing our crystallographic data for U(IV) and U(V) analogs, we noted that the pentavalent uranium phases, $3KF \cdot UF_5$, $3RbF \cdot UF_5$, and $3CsF \cdot UF_5$, were apparently isostructural with their tetravalent analogs, $3KF \cdot UF_4$, $3RbF \cdot UF_4$, and $3CsF \cdot UF_4$, and were of nearly identical unit cell size. To see whether this was a general phenomenon, we synthesized the previously unknown U(III) analogs.

The several UF_3–alkali fluoride compounds were synthesized under anhydrous conditions by the reaction of uranium metal, alkali fluoride, and UF_4 at temperatures of approximately 1000°. A double-chambered reactor was used with one chamber mounted over the other and separated by a ball valve. Each chamber could be evacuated independently and refilled with inert gas. The upper chamber held uranium metal. Melting, purification, and reduction of the uranium(IV) fluoride took place in the bottom nickel chamber. Stoichiometric amounts of UF_4 and the alkali fluoride were first loaded into the lower chamber and melted with $NH_4F \cdot HF$ in a dry helium atmosphere. After volatile phases were removed by distillation, the ball valve separating the two chambers was opened and the uranium metal suspended in the melt. The melted reaction mixture was stirred continuously with helium gas. Freshly prepared specimens of the complex fluorides of UF_3 were examined immediately after preparation, using polarizing microscopic methods, X-ray diffraction, and absorption spectrum (400 to 1500 mμ) measurements. The results of the optical analyses indicated that tetravalent uranium was either absent or of lower concentration than can be detected by this method. The U(III) compounds are readily oxidized to U(IV) compounds and must be protected from moist air.

The current investigation has demonstrated that reaction of UF_3 with the alkali fluorides yields many complex compounds of U(III). Those found have $MF{:}UF_3$ ratios of 1:1 for $M = Na^+, K^+, Rb^+$, or Cs^+; 2:1 (except for Na^+); and 3:1 (except for Na^+). No complex compounds of UF_3 are formed with LiF.[13b] Results obtained with $3KF \cdot UF_3$, $3KF \cdot UF_4$, and $3KF \cdot UF_5$ are listed in Table I; other results will be reported when the investigation is completed. On the basis of these findings, isomorphic complex fluorides may therefore be anticipated in the 4+ and 5+ states of Pa, in the 3+, 4+, and 5+ oxidation states of Pu and Np, as well as for the heavier actinides.

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Table I. X-Ray and Optical Crystallographic Properties

$3KF\cdot UF_3$[a]	$3KF\cdot UF_4$[b]	$3KF\cdot UF_5$[c]	$3KF\cdot PaF_5$[d]
Cubic	Cubic	Cubic	fcc
$a_0 = 9.2$ A	$a_0 = 9.2$ A	$a_0 = 9.2$ A	$a_0 = 9.2$ A
1.44[e]	1.436[e]		
Purple–brown	Green		

[a] This work. [b] References 11–13a. [c] Reference 7. [d] Reference 5. [e] Refractive index.

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Received Febuary 14, 1966

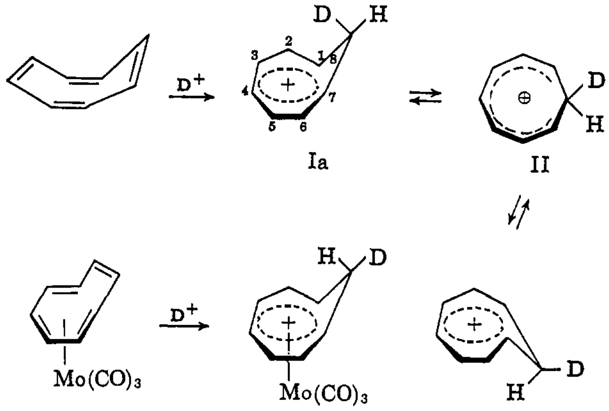
Ring Inversion, Ultraviolet Spectrum, and Electronic Structure of the Monohomotropylium Ion[1,2]

Sir:

The nmr spectrum of the $C_8H_9^+$ ion from protonation of cyclooctatetraene points clearly to the homoaromatic monohomotropylium structure I for this species.[3] This is true also of its molybdenum tricarbonyl complex IV.[3b] We now report on the rate of ring inversion in the monohomotropylium ion and the free-energy difference between this nonclassical species and a classical cyclooctatrienyl cation II. Further insight into the nature of I is provided by its ultraviolet spectrum in comparison with that of tropylium ion V.

Whereas protonation of cyclooctatetraenemolybdenum tricarbonyl (III) in D_2SO_4 is stereospecific,[3b] protonation of cyclooctatetraene (C_8H_8) appeared from earlier reports[3] not to be so. Solutions of C_8H_8 in D_2SO_4 showed *ca.* equal signals for "inside" and "outside" protons,[3a] and the sharpness of these signals made it evident[3b] that k for exchange of magnetic environments between these protons is less than 5 sec^{-1}.

When C_8H_8 is dissolved in D_2SO_4 at lower temperatures ($-10°$) and the nmr spectrum of the solution observed sooner than in the previous work, considerable tendency toward stereospecificity in the protonation step is evident, since about 80% of the incoming deuterium is "inside" (Ia). Thus, the stereospecificity is in the opposite direction from that in the protonation[3b] of C_8H_8–$Mo(CO)_3$ or the CO-evolving protonation[4,5] of C_8H_8–$Mo(CO)_4$. As the observation of the solution of C_8H_8 in D_2SO_4 is continued, the intensities of the inside and outside proton signals approach the value corresponding to half a proton in each position, thus permitting the evaluation of a first-order rate constant for the Ia → Ib isomerization. This is 9.8×10^{-4} sec^{-1} at *ca.* 37° and 6.1×10^{-4} sec^{-1} at *ca.* 32°, corresponding to a ΔF^* of 22.3 kcal/mole. If the Ia → Ib equilibration is visualized to proceed by ring inversion through a planar form, that of the classical cyclooctatrienyl cation (II), then the free energy of II is shown to be 22.3 kcal/mole higher than that of the homoaromatic monohomotropylium ion (I).



Ia II III IV Ib

Solutions of C_8H_8 in H_2SO_4 display a reproducible ultraviolet spectrum[6] resembling that of tropylium ion. The two λ_{max} values, 232.5 mμ (log ϵ 4.52) and 313 mμ (log ϵ 3.48), are at higher wavelengths than those for tropylium ion,[7] 217 mμ (log ϵ 4.61) and 273.5 mμ (log ϵ 3.63). Very illuminating is the fact that the λ_{max} for ultraviolet absorption of the homotropylium species I resembles more closely the value for tropylium ion V, with an HMO excitation energy of 1.692β, than the value to be expected for a classical planar cyclooctatrienyl species II with negligible 1,7 interaction. The HMO excitation energy for such an ion is 0.765β, and Deno[8a] has reported λ_{max} at 470 mμ for an actual heptatrienyl cation which could be taken as a model for II.

An estimate can be made of the value of the 1,7-resonance integral (β_{17}) in the homotropylium ion from the position of the long-wavelength ultraviolet absorption maximum at 313 mμ. It has been demonstrated that, for a large number of carbonium ions, a reasonably good correlation exists between the HMO excitation energy and the frequency of long-wavelength absorption.[9] In order that homotropylium fit such a correlation which includes Streitwieser's cations and five additional cations, allylic,[8a] pentadienyl,[8a] benzenium,[8b] and heptatrienyl[8a] in type, its HMO excitation energy must be approximately $1.45\beta_0$ which corresponds to $\beta_{17} = 0.73\beta_0$.[10,11] With this β_{17}, the 1,7 bond order is given as 0.56 by the HMO treatment, compared to 0.69, 0.62, and 0.65 for the π-electron 1,2, 2,3, and 3,4 bond orders, respectively. This is to be compared with a π bond order of 0.64 in tropylium ion.

The tropylium-like electronic description of the monohomotropylium ion (I), with a relatively even electron distribution around the C_1–C_7 carbon atom framework, is in good accord with the general features

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(1) Reported in part at the Kekulé Celebration Meeting of the German Chemical Society, Bonn, Germany, Sept 14, 1965.

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