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NOTE

SPECTRA, STRUCTURES, AND BONDING OF SOME URANIUM(IV) CYCLOPENTADIENYLS

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We report in this paper some data on tetracyclopentadienyluranium, UCp_4, tricyclopentadienyluranium chloride, UCp_3Cl, and tricyclopentadienyluranium tetrahydroborate, UCp_3BH_4 ($Cp = C_5H_5$). Some mention will also be made of the tricyclopentadienyluranium ion, UCp_3^+. Both UCp_3Cl and UCp_4 have been previously reported[1,2] and our data supplement the literature. The preparation and properties of UCp_3BH_4, reported only in a dissertation[3], are described and discussed.

EXPERIMENTAL

Syntheses

Preparative reactions were performed in a dry nitrogen atmosphere. Tetrahydrofuran was distilled from $LiAlH_4$ and purged with dry N_2 before use; benzene was treated successively with H_2SO_4, H_2O, NaOH, and H_2O, distilled from P_4O_{10}, and purged with dry N_2.

Uranium tetrachloride, from which all other compounds were synthesized, directly or indirectly, was prepared by the procedure of Hermann and Suttle[4] in which the orange modification of uranium trioxide was treated with hexachloropropene. Orange UO_3, in turn, had been prepared by a method essentially similar to that used by Selbin *et al.*[5]

Tricyclopentadienyluranium chloride was prepared by stirring UCl_4 with the theoretical amount of TlCp (Alfa Inorganics, Inc.) for 1–2 h either in THF at room temperature or in benzene under reflux. The product mixture was filtered to remove insoluble TlCl, solvent removed *in vacuo*, and dark brown UCp_3Cl isolated (90% yield) from the residue by sublimation at 210° and *ca.* 10^{-4} mm.

Tetracyclopentadienyluranium was synthesized in *ca.* 20% yield by treatment of UCl_4 in refluxing THF with a 2.5-fold excess of NaCp. This was followed by careful removal of the solvent under vacuum and sublimation at 195° and 10^{-4} mm of the bright red UCp_4.

A typical synthesis of UCp_3BH_4 was as follows: To a freshly prepared solution containing 1.3 mmoles of UCp_3Cl in 125 ml of THF was added 0.114 g (3.0 mmoles) of $NaBH_4$. Stirring of the reaction mixture at room temperature for 16 h followed.

$$UCp_3Cl + NaBH_4 \rightarrow UCp_3BH_4 + NaCl$$

The NaCl and excess $NaBH_4$ were removed by filtration through fine sintered glass; solvent was removed from the filtrate *in vacuo* at room temperature. The resultant brown solid then was sublimed at 170° and 10^{-4} mm to produce red-orange, crystalline UCp_3BH_4 in 95% yield. Identification of the product as UCp_3BH_4 was done by mass spectrometry.

Spectra

Visible and near-infrared spectra from 400 to 2600 nm for UCp_3Cl and UCp_3BH_4 and from 400 to 1400 nm for UCp_4 and UCp_3^+ (UCp_3Cl in deoxygenated H_2O) were obtained on a Cary Model 14 spectrophotometer with stoppered 1-cm silica cells. Infrared spectra of UCp_3Cl, UCp_4, and UCp_3BH_4 were obtained on KBr pellets in the range of 4000–250 cm^{-1} using a Perkin–Elmer Model 521 spectrometer.

Mass spectral measurements were recorded using a C.E.C. Model 21–110B double-focusing spectrometer equipped with a direct probe inlet. Typical conditions for UCp_3Cl, *e.g.* were probe temperature 120°, block temperature 170°, and pressure 1×10^{-6} mm.

RESULTS AND DISCUSSION

Electronic spectra

The visible spectra of UCp_3Cl and UCp_3^+ from 400–800 nm have been presented by Reynolds and Wilkinson[1]. Our spectra of these species agree with the reported spectra, except from about 750–800 nm where it appears that the detector of the instrument used by the former workers may have been insensitive.

Molar extinction coefficients for UCp_3BH_4 are about a factor of two larger than values in the same wavelength regions for UCp_3Cl[1], *viz.* in 7.0×10^{-4} *M* UCp_3BH_4, $\varepsilon = 390$ at 533 nm and 200 at 747 nm. No extinction coefficients were determined for UCp_4 due to rapid decomposition of the compound on manipulation of its solutions.

Except for the strong shoulder peaks at 425 and 510 nm, the absorption bands for UCp_4 appear weak relative to those for the other uranium cyclopentadienyl compounds; this may be due to the symmetrical tetrahedral structure[2] of the former. Thus, using arguments analogous to those of Gans *et al.*[6], it is suggested that the tetrahedral symmetry of UCp_4 is destroyed by substituting for one Cp ligand such non-equivalent ligands as H_2O, BH_4, or Cl. Although exact structures of UCp_3BH_4 (in C_6H_6) and the aquated $UCp_3(H_2O)_x^+$ species are unknown, a single crystal study of UCp_3Cl has shown it to be a distorted tetrahedron with a monoclinic crystal structure[7]. It is of interest here that X-ray powder pattern data indicate that none of the compounds, UCp_4, UCp_3BH_4, or UCp_3Cl, as well as the n-butoxide, $UCp_3OC_4H_9$, reported by Ter Haar and Dubeck[8], are isomorphous.

Term assignments of all major peaks in the visible near-infrared spectra of our uranium cyclopentadienyl compounds have been made and are given in Table 1. The assignments are based mainly on the various spectra of U^{IV} compounds reported by Gans *et al.*[6] and can be interpreted in terms of $5f^2$ electronic configurations for the uranium atom in the cyclopentadienyls. Some of the absorption bands in the table, especially those assigned to the $^3P_0$ and $^3F_3$ terms, are generally somewhat lower in frequency than values reported for other U^{IV} species[6].

TABLE 1. ELECTRONIC SPECTRAL WAVENUMBERS AND TERM ASSIGNMENTS

UCp_3Cl	UCp_3BH_4	UCp_3^+	UCp_4	Term assignment
n.d.[a]	n.d.	n.d.	n.d.	$^1S_0$
n.d.	n.d.	23240	23534	$^3P_2$
21584	21834	21101		$^1I_6$
19697	20024	19670	19585	
18389	18758	17274	17209	$^3P_1$
16784	17106	16518	16852	$^1D_2$
15449	15044	15149		$^1G_4$
14890			14310	
14203				$^3P_0$
14049				
13818	13390	12183	13142	
10806	10126	10966	10924	$^3H_6$
	10042			
9889		9819	9834	$^3F_4$
9701		9618		
9479	8943		8482	
8811	8538		8354	
8284	8074	7846	7899	$^3F_3$
7717		7705		
7514			7374	
6198	6513	n.d.	n.d.	$^3H_5$
6051	6445			
4252	4060	n.d.	n.d.	$^3F_2$
0	0	0	0	$^3H_4$

[a] Not determined.

Mass spectra

The mass spectrum of UCp_4 at 70 eV appears normal in that the first Cp ligand is readily removed but the remaining ligands are increasingly difficult to strip off. In the case of UCp_3Cl, the ionic[1,3,7] U–Cl bond is more difficult to rupture than the more covalent U–C bond(s). However, a parallel in the mass spectra of UCp_4 and UCp_3Cl is evident in the nearly constant relative intensity values found for the UCp_x^+ ions for UCp_4 and the corresponding $UCp_{x-1}Cl^+$ ions (where $x=3$, 2, or 1, respectively) from UCp_3Cl. Thus, mass spectra are insensitive to the proposed[3] trend in U–Cp bond character from the more ionic UCp_4 to the more covalent UCp_3Cl.

The fragmentation pattern of the tetrahydroborate appears somewhat unusual with the most intense peak that for the UCp_2^+ ion, *i.e.* an ion resulting from the loss of two substituents rather than one. That this is not caused by the high ionizing voltage was shown in that even at 15 eV the UCp_2^+ ion was the most prominent and all other fragment ions were relatively weak in intensity. Thus, under the conditions of the mass spectrometer, the U–C bond(s) in UCp_3BH_4 are generally stronger than the $U–BH_4$ bond. Our results on UCp_3BH_4 are similar in some respects to the mass spectral cracking pattern of the compound $ZrCp_2(H)BH_4$[9] from which it was suggested that the ion $ZrCp_2^+$ is particularly stable. In addition, these authors report a weak parent ion in the mass spectrum of $ZrCp_2(BH_4)_2$.

Infrared spectra

Our infrared spectra of UCp_3Cl, UCp_4, and UCp_3BH_4 from 4000–667 cm^{-1}

agree reasonably well with the literature[1-3]. In the far infrared region the following absorption bands (cm^{-1}) and relative intensities were found: UCp_3Cl, 594 w and 298 vw; UCp_4, 609 s and 593 s; UCp_3BH_4, 415 w, 332 m, and 260 m. The bands in the 300 cm^{-1} region are likely due to metal–Cp ring stretching while those near 600 cm^{-1} may arise from out-of-plane ring deformations[10]. Additional possible significance of the strong doublet at 609 and 593 cm^{-1} for UCp_4 must await reports of similar spectra for other metal cyclopentadienyls.

In the C–H-stretching region, UCp_3Cl gives rise to only the asymmetric band at 3068 cm^{-1}, while UCp_3BH_4 and UCp_4 each show, in addition, a symmetric stretching band near 2925 cm^{-1}. Although Hristidu reported[3] a band at 2924 cm^{-1} for UCp_3Cl, we found, in agreement with earlier workers[1], that such a band can arise from decomposition. The absence of a symmetric C–H-stretching band may thus indicate predominantly π-U–Cp bonding in UCp_3Cl[11]. The metal–Cp ring bands in UCp_4 and UCp_3BH_4 may, therefore, possess some degree of σ character. This is in general agreement with Hristidu[3], who claimed a decreasing degree of ionic character in the series UCp_4, UCp_3, UCp_3BH_4, UCp_3Cl, and $UCp_3OC_2H_5$.

Band positions of the BH_4 ligand in UCp_3BH_4 compare closely with those reported for $ZrCp_2(BH_4)_2$[12] but differ significantly from the spectrum of $TiCp_2BH_4$[13], *e.g.* the asymmetric B–H bridge stretching frequency is estimated from the spectrum of the titanium compound to be 2041 cm^{-1}, or over 100 wavenumbers lower than the corresponding frequencies for UCp_3BH_4 (2142 cm^{-1}) and $ZrCp_2(BH_4)_2$ (2149 cm^{-1}). Additionally, a strong Ti–H stretching band is reported at 1942 cm^{-1} but analogous metal–hydrogen bands are absent in the spectra of the uranium and zirconium compounds. Therefore, UCp_3BH_4 is probably nearer to the double-hydrogen bridged structure proposed[14] for $ZrCp_2(BH_4)_2$ as opposed to the Ti–H bond and coordinated BH_3 group suggested[13], but not proven unequivocally, for $TiCp_2BH_4$.

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