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THE SYNTHESIS AND CHARACTERIZATION OF (UCp3) 2 (PYRAZINE) AND [U (MeCp) 3]2 (PYRAZINE) : n -BRIDGED DIMERS OF U3+

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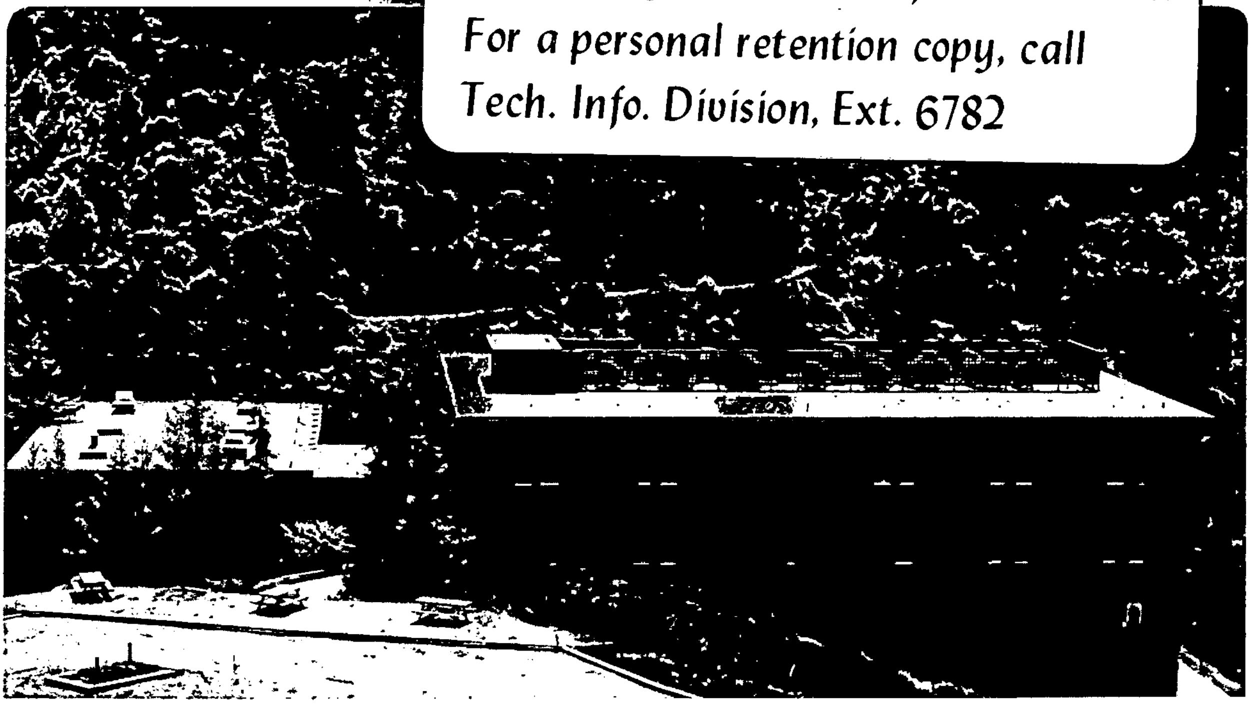

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The Synthesis and Characterization of $(UCp_3)_2$(pyrazine) and $[U(MeCp)_3]_2$(pyrazine): π-Bridged Dimers of U^{3+}

By

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Abstract

The title compounds are formed by the raction of $U(C_5H_5)_3(C_4H_8O)$ and $U(C_6H_7)_3(C_4H_8O)$ with pyrazine $(C_4H_4N_2)$ and characterized by elemental analysis, mass, infrared, ^1H nmr, and electronic spectra, and by X-ray powder patterns. The $[U(C_6H_7)_3]_2(C_4H_4N_2)$ exhibits anomalous magnetic behavior that remains under investigation.

Introduction

Since the resurgence of interest in the organometallic chemistry of the lanthanide and actinide elements in the 13 years since the synthesis of uranocene [1], a continuing question has been the role of f-electrons in the bonding in these compounds [2]. As part of a program to create, examine, and explain structural and magnetic probes of this bonding [3,4], we have sought the synthesis of appropriate dimeric species of uranium for detailed magnetic characterization. A previous report on the synthesis and characterization of $(YbCp_3)_2$(pyrazine) led to the conclusion that as low as 4K no spin-pairing took place [4]. The behavior of pyrazine in d-metal dimers has demonstrated that, in the covalent extreme, it can facilitate spin-pairing between the metal ion paramagnets. The fact that no pairing was apparent in the Yb complex is convincing evidence of the predominantly ionic bonding in this compound, consonant with the known core-like properties of the 4f shell.

However, in the early actinides the 5f shell electrons make a greater contribution to the chemical environment, and so dimeric compounds of uranium have been sought. A few other uranium dimers have been reported [5], but their magnetic characterization has not been complete. This study represents the completion of the investigation of the f-dimer complexes of pyrazine that began with $(YbCp_3)_2$(pyrazine) compound.

Experimental

All manipulations were accomplished using a Schlenk or vacuum line with high pruity Argon or in a Vacuum Atmospheres HE-93 glove box with a recirculating oxygen and moisture-free Argon atmosphere. All solvents were dried by distillation from potassium benzophenone ketyl and were degassed prior to use. Pyrazine (Aldrich 99+%) was dried over BaO at 60°C. Infrared spectra were recorded on a Perkin-Elmer 597 spectrophotometer, the visible-near IR spectra on a Cary 14M spectrophotometer, nmr spectra on the UCB 250 MHz spectrometer, and mass spectra on an AEI-MS12 spectrometer. The magnetic behavior was measured as described elsewhere [3]. Elemental analyses were performed by the Microanalytical Laboratory at the University of California, Berkeley; or Mallissa and Reuter Analytische Laboratorien, Engelskirchen, West Germany. The X-ray powder patterns were collected with Cu radiation. The NaCp(DME) [6] (DME is 1,2-dimethoxyethane) and UCl_4 [7] were prepared by the literature techniques. Napthalene was sublimed before use. The K(MeCp) was produced by the reaction between the diene (after cracking) and KH in THF (tetrahydrofuran) at 0°C.

$UCp_3(THF)$ and $U(MeCp)_3(THF)$. To small pieces of sodium weighing 0.30 g (13 mmol) in 100 mL THF was added 1.70 g (13 mmol) of napthalene. The resulting dark green mixture was stirred at room temperature overnight. It was then filtered through a glass frit onto 5.00 g (13 mmol) of UCl_4 in 150 mL THF. The mixture of green solutions turned immediately to a deep purple. This mixture was stirred at room temperature for one hour. Next, the NaCp(DME) or KMeCp (39.5 mmol) (solution and slurry, respectively) in 100 mL THF was added, the purple changing to brown immediately. This mixture was stirred at room temperature for another hour, at which time the THF was removed under vacuum. Care was taken to retain a slight dampness of THF. The brown residue was soxhlet extracted with benzene overnight. Next the benzene was removed under vacuum and the residue subjected to room temperature vacuum for 12 hours to remove the napthalene. The product thus obtained (90% based on UCl_4) is crystalline. Its composition was confirmed by the IR spectrum [8], pmr spectrum [for the methylated compound at 21°C in d^8-toluene, shifts in δ ppm versus TMS: -8.1 (s, $\sim$ 7 H, 102 Hz); -14.5 (s, $\sim$ 12 H, 49 Hz); -21.4 (s, $\sim$ 8 H, 73 Hz)], and elemental analysis.

Anal. Calcd for $UC_{22}H_{29}O$: C, 48.26; H, 5.30;
Found: C, 48.91; H, 5.53.

$(UCp_3)_2$(pyrazine). This compound can be synthesized by the combination of stoichiometric amounts of UCp_3(THF) and pyrazine in benzene, toluene, DME, or THF. The blue-grey product precipitates immediately upon addition of pyrazine to a brown solution of UCp_3(THF). It is most soluble in THF, but only sparingly so. The supernatant from a THF preparation, if cooled quickly to -78°C and held there for a few days, yields black microcrystalline material. This material was used for the X-ray powder pattern.

Anal. Calcd. for $U_2C_{34}H_{34}N_2$: C, 43.13; H, 3.59; N, 2.96.
Found: C, 43.40; H, 4.07; N, 2.22.
Infrared spectrum (Nujol mull)(cm^{-1}) 3080, 1422, 1279, 1261, 1068, 1018, 960, 809, 782, 737, 619, 602, 470.
Mass spectral data (70 eV) are included in Table Ia.

The low solubility of this compound hampered further characterization.

$[U(MeCp)_3]_2$(pyrazine). To a dark brown solution of $U(MeCp)_3(THF)$ in toluene was added a stoichiometric amount of pyrazine in a small volume of toluene. The color changed immediately to a deep blue-black. Stirring at room temperature for a few minutes, followed by filtration yielded a very strongly colored filtrate. Cooling to -15°C overnight yielded black crystals shaped like needles.

Anal. Calcd. for $U_2C_{40}H_{46}N_2$: C, 46.29; H, 4.28; N, 2.81.
Found: C, 46.60; H, 4.47; N, 2.72.

Infrared spectrum (Nujol mull)(cm^{-1}) 1420, 1279, 1057, 1048, 1030, 950, 880, 849, 840, 805, 770, 758, 742, 728, 694, 611, 463.

PMR spectrum (20°C, d^8-toluene, δ ppm versus TMS) -2.15 (s, 18 H, 9 Hz, Me); -11.5 (s, 11 H, 15 Hz, ring); -13.4 (s, 12 H, 15 Hz, ring); -67.0 (s, 4 H, 15 Hz, pyrazine).

Mass spectral data (70 eV) are in Table Ib.

Electronic spectrum (in toluene versus toluene)(nm) 1510, 1360, 1220, 1180, 1020, 910, 680. The maxima are quite broad.

Single crystals suitable for diffraction studies have not been obtained. Both this and the previous compound sublime with some decomposition at 10^{-3} torr and 120°C.

Discussion

The dimeric formulation of these compounds is based primarily on: (a) the X-ray power pattern of $(UCp_3)_2$(pyrazine); (b) the mass spectra of both compounds; and (c) the pmr of the methylated compound.

The crystal and molecular structure of $(YbCp_3)_2$(pyrazine) has been determined [4], and consists of a dimer located about a crystallographic inversion center. Two ytterbium atoms, each with three η^5-Cp rings, are nearly linearly bridged by a pyrazine ring coordinated through its nitrogens. Because $(UCp_3)_2$(pyrazine) exhibits low solubility, and $[U(MeCp)_3]_2$(pyrazine) forms only thin needles during crystal growth, a single crystal X-ray structure of these compounds has eluded us. However, it is reasonable to assume that substitution of U^{3+} for Yb^{3+} would lead to isomorphic structures, and if so, that powder patterns of the two compounds should be quite similar. Indeed this is so, the similarity of the patterns extending to the general pattern of the lines and their relative intensities.

The mass spectra of both compounds reveal the presence of dimeric species (Table I). Both spectra contain several prominent peaks that are not easily assigned, but that are included for completeness. The intensity of the high-mass peaks is rather low, consistent with the decomposition observed during sublimation. In the spectrum of the methylated compound, peaks appear that correspond to $[U_2L_{6-x}$(pyrazine) + $15]^+$, which suggests that perhaps uranium-methyl bonds are formed in the spectrometer.

The pmr spectrum of the methylated compound includes one singlet resonance for the four pyrazine protons. This supports the dimer formulation since in the monomer the chemical shifts should be two sets of two. This spectrum also exhibits resonances one expects for the mono-methylCp ligands — the methyl groups shifted the least, while the inequivalent sets of ring protons are shifted more by the uranium ion.

Our use of the liquid helium apparatus is predicated on the expectation that any covalent effects would be of particularly low energy and necessitate the use of very low temperatures. For this reason neither the room temperature moment nor the temperature dependence of the nmr spectrum has been determined. The magnetic behavior of the methylated compound has been investigated four times. Three times the data indicate the compound is only weakly paramagnetic, and that the paramagnetism varies slowly with temperature. The fourth investigation produced results that suggest an abrupt spin-state change at very low temperature. Any further interpretation of the magnetic behavior of this compound will require further investigation.

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Table Ia. Mass spectrum of $(UCp_3)_2$(pyrazine).

RA (%)[a]	m/e	Assignment[b]
0.8	883	U_2L_5X
1.5	817	U_2L_4X
0.8	620	U_2LX
1.1	514	UL_3X
1.4	512	-
15	433	UL_3
16	403	-
25	387	-
22	368	UL_2
16	338	-
23	322	-
4	303	UL
72	80	X
73	66	L
100	44	-

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[a] Relative abundance.

[b] $L = C_5H_5$ and $X = C_4H_4N_2$.

Table Ib. Mass spectrum of $[U(MeCp)_3]_2$(pyrazine).

RA (%)[a]	m/e	Assignment[b]
0.2	966	$U_2L_5X + 15$
0.1	952	U_2L_5X
0.7	887	$U_2L_4X + 15$
0.4	873	U_2L_4X
0.3	726	-
0.6	647	-
0.7	602	-
0.7	568	-
2.0	556	UL_3X
1.5	523	-
30	494	-
20	475	UL_3
25	431	-
88	415	-
40	336	-
70	80	X
100	79	L

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[a] Relative abundance.

[b] $L = C_6H_7$ and $X = C_4H_4N_2$.

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