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Preliminary communication

CYCLOPENTADIENYLDICHLOROURANIUM HYDROTRI-1-PYRAZOLYLBORATE, $CpUCl_2[HBPz_3]$

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Summary

The mixed sandwich compound $CpUCl_2[HBPz_3]$ has been prepared by treatment of $CpUCl_3 \cdot 2THF$ with the stoicheiometric amount of $K[HBPz_3]$ in THF; the IR and ^1H NMR spectra are discussed.

Complexes in which the metal atom is bonded to poly-1-pyrazolylborate as well as to a h^5-cyclopentadienyl ligand are known for a few *d*-transition metals [1] but have not been recorded for the actinide elements. We have recently [2] reported the preparation of a number of uranium(IV) poly-1-pyrazolylborate complexes and we now describe the first uranium compound in which both h^3-hydrotri-1-pyrazolylborate and h^5-cyclopentadienyl ligands are bonded to the metal.

Experimental

All work was carried out in dry atmosphere, nitrogen filled gloveboxes because of the oxygen and moisture sensitivity of the compounds.

The starting material, $CpUCl_3 \cdot 2THF$, was prepared by the method reported for $CpUCl_3 \cdot DME$ except that THF was used as the solvent [3]. (Found: C, 27.3; H, 3.8; Cl, 19.8; U, 44.3. $C_{13}H_{21}O_2UCl_3$ calcd.: C, 28.3; H, 3.8; Cl, 19.3; U, 43.1%). $CpUCl_3 \cdot 2THF$ (0.935 g) was then mixed with $K[HBPz_3]$ (0.428 g, 1 eq.) and dry THF (30 ml). After stirring for 48 h at room temperature the suspension was centrifuged to remove KCl and the green supernatant was evaporated to dryness in vacuo. The resulting green solid was heated at 100°C for 1 h at 10^{-3} mm Hg and then sublimed at 220°C/10^{-3} mm Hg onto a water-cooled cold finger (yield ~ 30%). (Found: C, 29.0; H, 2.7; Cl, 11.8; U, 40.2. $C_{14}H_{15}BCl_2N_2U$ calcd.: C, 28.6; H, 2.6; Cl, 12.1; U, 40.6%). The analytical results were obtained as described previously [2].

Spectra

IR spectra were recorded using a Perkin—Elmer PE 257 spectrometer (4000—625 cm^{-1}) with samples mounted as mulls in Nujol between NaCl plates. ^{1}H-NMR spectra were recorded using a Varian HA100 (100 MHz) or a Perkin—Elmer R12 (60 MHz)spectrometer using tetramethylsilane as external standard.

Results and discussion

$CpUCl_3 \cdot 2THF$ is a bright-green, air-sensitive solid which decomposes in acetone, benzene and upon heating above 120°C. IR spectroscopy showed that the THF in the molecule is not liberated at 70°C/10^{-3} mm Hg; its IR spectrum exhibits features at 3010, 1015, 830 and 795 cm^{-1} characteristic of cyclopentadienyl groups, and features due to THF appear at 1000 and 920 cm^{-1}. The ^{1}H NMR spectrum (in THF-d_8) exhibits a resonance due to C_5H_5 protons at 692 Hz, the THF resonances being obscured by the presence of undeuterated THF in the THF-d_8 used as solvent. The two molecules of THF are presumably bonded to $CpUCl_3$ so achieving the same coordination number for uranium as in the known [3] DME complex.

$CpUCl_2[HBPz_3]$ is a bright-green, air-sensitive solid which is soluble in acetone and THF, but is insoluble in dichloromethane. Its IR spectrum exhibits a B—H stretching mode at 2500 cm^{-1}, features at 1015 and 820 cm^{-1} characteristic of cyclopentadienyl groups and all the features characteristic [2] of the pyrazolylborate group are also present. The U—Cl stretching vibration appears as a broad band centred at 255 cm^{-1} compared with 270 cm^{-1} in $UCpCl_3 \cdot 2THF$; the band observed at 330 cm^{-1} is probably due to the uranium—nitrogen bond, since it is absent in the spectrum of $CpUCl_3 \cdot 2THF$. The UV/visible spectrum of the complex in THF exhibits intense bands at 490, 570, 600, 680, 1160 and 1460 nm which are consistent with low symmetry, high ($\geqslant$ 8) coordination uranium(IV) species. The ^{1}H NMR spectrum (in THF-d_8), and the integration data are given in Table 1.

TABLE 1

^{1}H NMR RESULTS FOR $CpUCl[HBPz_3]$

Resonance (Hz) [a]	J(Hz)	Proton integration
659.2(d)	7.2	5
694.3(s)		3
732.2(s)		1
2220.0(s)		3
3110.0(s)		3

[a] s, singlet; d, doublet.

The resonances at 3110, 2220 and 694.3 Hz can be assigned to H(3), H(4) and H(5) respectively of the pyrazolyl ring and the resonance at 659.2 Hz, although clearly split into a doublet, is undoubtedly due to the cyclopentadienyl group protons. The resonance at 732.2 Hz can be assigned to the boron proton; it should be noted that this last resonance is shifted by the same amount [2] in the ^1H NMR spectrum of $UCl_2[HBPz_3]_2$. The assignments indicate that the $[HBPz_3]$ group is acting as a tridentate ligand in $CpUCl_2[HBPz_3]$ in contrast to $UCl_2[HBPz_3]_2$ [2] in which it appears to be only bidentate. The very large chemical shifts for the pyrazole ring protons H(3) and H(4) are paralleled by similar shifts for H(3), 2130 Hz, and H(4), 754 Hz, in $UCl_2[HBPz_3]_2$, behaviour which can be expected for compounds containing a paramagnetic metal ion, such as U^{IV}.

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