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Uranium(IV) Bishydrotris(pyrazol-1-yl)boratothiolato Derivatives*

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Although extensive studies of the chemistry involving metal–sulphur bonds have been made for d-transition elements, for the actinides fewer reports have been published. Among them we refer here to the chelated diethyldithiocarbamates of quadrivalent actinides (Th, U, Np, Pu) [1, 2], and some thiol derivatives prepared using the complex $Cp_2U[N(C_2H_5)_2]_2$ [3] (where Cp = cyclopentadienide) as precursor.

In our laboratories we have studied recently the reactivity of $U[HBpz_3]_2Cl_2$ and we obtained a series of compounds of the type $U[HBpz_3]_2R_x(Cl)_{2-x}$ (pz = pyrazol-1-yl; $x = 1$ or 2 and R = OBu^t, OPr^i and OC_6H_2-2,4,6-Me_3 [4].

In the present work we describe the reactions of the fairly reactive and stable precursor, $U[HBpz_3]_2Cl_2$ [5] with $NaSBu^t$ in the molar ratios of 1:1 and 1:2. ^1H NMR studies were made to investigate the dynamic properties of the bisthiolato complex.

Experimental

All operations were carried out with exclusion of oxygen and moisture in a nitrogen-filled glove box or using Schlenk and vacuum line techniques. All solvents were dried, distilled and degassed prior to use.

$NaSBu^t$ was prepared by reaction of $HSBu^t$ with equimolar amounts of Na in tetrahydrofuran (thf).

$U[HBpz_3]_2Cl_2$ was synthesized as previously described [5].

$U[HBpz_3]_2[SC(CH_3)_3]_2$ was prepared as follows. 400 mg (0.54 mmol) of $U[HBpz_3]_2Cl_2$ and 120 mg (1.08 mmol) of $NaSBu^t$ in thf (10 ml) were stirred overnight at room temperature. The suspension was centrifuged and the red solution was vacuum dried. The red solid obtained was washed with n-pentane and dried (yield, 85%). *Anal.* Calc. for $U[HB(C_3H_3N_2)_3]_2[SC(CH_3)_3]_2$: N, 19.95; C, 37.06; H, 4.51. Found: N, 19.83; C, 37.31; H, 4.42%.

The electronic absorption spectrum in toluene or in thf gave (nm): 673(m); 690(m); 1100(s); 1124(sh); 1167(sh); 1212(w); 1369(broad and m). The infrared spectrum (Nujol mull): ν (B–H) mode 2460 cm^{-1}.

Results and Discussion

The complex $U[HBpz_3]_2Cl_2$ reacts readily with $NaSC(CH_3)_3$ in thf in the ratio 1:2 to give the red bisthiolato complex $U[HBpz_3]_2[SC(CH_3)_3]_2$ (**I**). This complex can be obtained in good yield (85%) and it is quite soluble in tetrahydrofuran, toluene, benzene and aliphatic hydrocarbons.

The ^1H NMR spectrum at 300 K of **I** in toluene-d_8 (Table I) displays for the protons of the poly(pyrazol-1-yl)borate ligands a pattern similar to the one we obtained, at 300 K, for the starting material as well as for the complexes of the type $U[HBpz_3]_2R_x(Cl)_{2-x}$ ($x = 1$ or 2 and R = OPr^i; $x = 1$ and R = OBu^t; $x = 2$ and R = OC_6H_2-2,4,6-Me_3 [4].

As we observed before, this pattern indicates that the pyrazol-1-yl rings are magnetically equivalent and this can be explained assuming a fluxional behaviour for these ligands which can be described as a non-dissociative trigonal twist mechanism (rotation of the ligands about the U–B axis) [6]. Thus, variable temperature ^1H NMR studies were made in order to estimate the barrier to rotation about the U–B axis.

Upon lowering the temperature we observed that the line shape of the resonance due to the protons of the thiolate ligands was temperature independent and the chemical shifts were found to obey an approximate Curie relationship. However, the line shapes of the signals due to the protons of the polypyrazol-1-yl ligands were temperature dependent and, after broadening, the collapse of the signal due to the H(3) protons was observed at 265 K and the collapse of the signals due to the H(4) and H(5) protons was observed at 255 K.

TABLE I. ^1H NMR Spectroscopic Data for $U[HBpz_3]_2[SC(CH_3)_3]_2$[a]

T (K)	$HBpz_3$	$SC(CH_3)_3$
300	29.1(6H, H(3)); 6.9(6H, H(4)); 0.8(6H, H(5)); −16.1(2H, (B–H))	11.6(18H)
215	72.7(2H); 59.1(2H); 17.6(4H); 7.1(4H); −15.5(2H); −19.9(4H); −23.2(2H)	13.9(18H)
190	83.6(2H); 62.5(2H); 22.6(2H); 16.6(2H); 8.7(2H); 5.4(2H); −16.9(2H); −21.9(2H); −23.7(2H) −25.4(2H)	14.6(18H)

[a] All the spectra were recorded in toluene-d_8; the chemical shifts are reported in ppm from tms; downfield shifts are positive.

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At 215 K the ^{1}H NMR spectrum showed seven signals for the protons of the pyrazol-1-yl borate ligands (Table I). Upon further lowering the temperature the resonance at 17.6 splits into two signals of intensity ratio 1:1; the same behaviour was observed for the resonances at 7.1 ppm and at −19.9 ppm. No further splitting of the signals was seen at lower temperatures and the limiting static spectrum at 190 K displayed ten resonances for the protons of the poly(pyrazol-1-yl)borate ligands (Table I). From the three sets of coalescing lines the free energy of activation at the coalescence temperature was estimated to be 40.0 ± 3.0 kJ mol^{-1}.

The pattern obtained for the limiting static spectrum at 190 K (Table I) was similar to the one we obtained for the complex $U[HBpz_3]_2(OBu^t)_2$ [4], but the barrier to rotation estimated for the bisthiolato complex was lower than the value estimated for the terbutoxide derivate ($\Delta G^{\neq} = 53 \pm 4$ kJ mol^{-1}).

If we assume that stereochemical factors play a dominant role in this process, it is reasonable to assume that the bisthiolato complex is a less congested molecule owing to the larger size of the sulphur atom which will remove the bulky Bu^t fragment to a larger distance from the metal centre than in the case of the alkoxide.

The reaction of the complex $U[HBpz_3]_2Cl_2$ (**II**) with one equivalent of $NaSBu^t$ led to a mixture of species. The ^{1}H NMR spectrum of this mixture indicated unequivocally that the species $U[HBpz_3]_2(SBu^t)_2$ (**I**) and $U[HBpz_3]_2Cl_2$ (**II**) were present. A third species was formulated as $U[HBpz_3]_2(SBu^t)Cl$ (**III**) on the basis of the ^{1}H NMR spectrum [27.3(6H, H(3)); 7.5(6H, H(4)); 1.6(6H, H(5)); −14.6(2H, broad (B–H)); 16.0(9H, $SC(CH_3)_3$)]. Complex **I** can be completely removed by repeated washing with n-pentane, but the remaining yellow solid still contains both **II** and **III** species. The ^{1}H NMR spectra showed that species **II** is stable in solution but the resonances due to the protons of species **III** vanished after some time, giving way to the absorptions characteristic of the free thiol.

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