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Synthesis and Characterization of $UCl_2[HB(3,5\text{-}Me_2pz)_3](3,5\text{-}Me_2pz)$ and $MCl_3[HB(3,5\text{-}Me_2pz)_3](3,5\text{-}Me_2pzH)$ (M = U(IV) and Th(IV); pz = pyrazolyl)

NOÉMIA MARQUES†, J. MARÇALO, A. PIRES DE MATOS

Departamento de Quimica, ICEN, LNETI, 2686 Sacavém Codex, Portugal

K. W. BAGNALL

Department of Chemistry, The University of Manchester, Manchester M13 9PL, U.K.

and J. TAKATS

Department of Chemistry, University of Alberta, Edmonton, Alberta, T6G 2G2, Canada

The reaction of MCl_4 with one equivalent of $KHB(3,5\text{-}Me_2pz)_3$ in thf (where pz = pyrazolyl, thf = tetrahydrofuran) gives the monosubstituted derivatives $MCl_3[HB(3,5\text{-}Me_2pz)_3](thf)$ [M = Th(IV) and U(IV)] as reported [1]. In contrast to the less bulky ligand $(HBpz_3)^-$, which can form the complexes $MCl_2(HBpz_3)_2$, the reaction of UCl_4 and $ThCl_4$ with two equivalents of $KHB(3,5\text{-}Me_2pz)_3$ led to mixtures of products, as shown by ^1H and ^{11}B NMR spectroscopy for uranium [2] and by ^1H NMR spectroscopy for thorium. In the latter case, the main product formed in the reaction was $ThCl_3[HB(3,5\text{-}Me_2pz)_3](thf)$. However, for uranium no product could be easily identified from the reaction mixture.

It has been previously reported from reactions involving Nb, Ta and Rh complexes [3, 4] that the ligand $[HB(3,5\text{-}Me_2pz)_3]^-$ can suffer cleavage, yielding as possible fragments $3,5\text{-}Me_2pzH$ and $(3,5\text{-}Me_2pz)^-$. This prompted us to investigate the reaction of $MCl_3[HB(3,5\text{-}Me_2pz)_3](thf)$ with one equivalent of either 3,5-dimethylpyrazole or sodium dimethylpyrazolide. From these reactions $MCl_3[HB(3,5\text{-}Me_2pz)_3](3,5\text{-}Me_2pzH)$ and $UCl_2[HB(3,5\text{-}Me_2pz)_3](3,5\text{-}Me_2pz)$ could be isolated and fully characterized. Comparative studies of these complexes and the reaction mixture referred to above were made using NMR and electronic spectroscopies and it was found that the main product from the reaction of UCl_4 with two equivalents of $KHB(3,5\text{-}Me_2pz)_3$ was $UCl_2[HB(3,5\text{-}Me_2pz)_3](3,5\text{-}Me_2pz)$. Work-up of the reaction mixture gave the pure compound. In the thorium case, no analogous complex was obtained.

Experimental

The preparation and handling of the compounds were carried out in a nitrogen-filled glove-box or using Schlenk and vacuum line techniques. All solvents were dried, distilled and degassed just prior to use.

3,5-Dimethylpyrazole was sublimed before use and sodium 3,5-dimethylpyrazolide was prepared by reaction of 3,5-dimethylpyrazole in thf with the stoichiometric amount of NaH. $MCl_3[HB(3,5\text{-}Me_2pz)_3](thf)$ complexes were prepared as previously reported [1].

Infrared spectra were recorded using a Perkin-Elmer 577 spectrophotometer in Nujol mulls sandwiched between CsI plates. Solution electronic spectra were recorded using a Cary 17 Varian spectrophotometer. Proton NMR spectra were recorded on a Bruker SY80FT multinuclear spectrometer. C, H, and N analyses were performed using a Perkin-Elmer automatic analyser.

Syntheses

$UCl_3[HB(3,5\text{-}Me_2pz)_3](3,5\text{-}Me_2pzH)$

To a solution of 190 mg (0.27 mmol) of $UCl_3[HB(3,5\text{-}Me_2pz)_3](thf)$ in thf (20 cm^3) were added 26 mg (0.27 mmol) of 3,5-dimethylpyrazole. After stirring for 36 h the green solution was evaporated to dryness, washed with n-pentane and vacuum dried to give a green powder.

$ThCl_3[HB(3,5\text{-}Me_2pz)_3](3,5\text{-}Me_2pzH)$

This was prepared in the same way as a white solid.

$UCl_2[HB(3,5\text{-}Me_2pz)_3](3,5\text{-}Me_2pz)$

(i) Addition of 30.4 mg (0.26 mmol) of sodium dimethylpyrazolide to a solution of 184 mg (0.26 mmol) of $UCl_3[HB(3,5\text{-}Me_2pz)_3](thf)$ in 10 cm^3 of thf led to an immediate colour change from bright to deep green. After stirring for 16 h the solution was centrifuged and the supernatant was evaporated to dryness giving a green oil. After stirring with n-pentane for 3 h a microcrystalline powder was formed.

(ii) To 415 mg (1.09 mmol) of UCl_4 in 20 cm^3 of thf were added, with stirring, 733.9 mg (2.18 mmol) of $KHB(3,5\text{-}Me_2pz)_3$. After stirring overnight the solution was centrifuged, the supernatant was evaporated to dryness and the residue was washed three times with toluene (3 × 5 cm^3), then with n-pentane and vacuum dried.

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†Author to whom correspondence should be addressed.

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Results and Discussion

$MCl_3[HB(3,5\text{-}Me_2pz)_3](3,5\text{-}Me_2pzH)$

Replacement of thf in $MCl_3[HB(3,5\text{-}Me_2pz)_3]$(thf) by 3,5-dimethylpyrazole was easily achieved by reaction of stoichiometric amounts of the appropriate reagents in thf solution. Analytical and physical data for the complexes are given in Table I and ^{1}H NMR data in Table II.

The uranium and thorium complexes display single signals for the methyl-3 and methyl-5 protons, and proton-4 of the pyrazolyl rings, indicating that the three rings are in magnetically equivalent environments, as was also observed previously for the compounds $MCl_3[HB(3,5\text{-}Me_2pz)_3]$(thf), indicating C_{3v} local symmetry. The same symmetry was also observed for the solid compound $UCl_3[HB(3,5\text{-}Me_2pz)_3]$(thf) as was proved by single crystal X-ray analysis. This molecule has a capped octahedral geometry with the thf capping the face defined by the three Cl atoms [1]. The similarity in structure of the dimethylpyrazole and thf adducts is also indicated by the electronic absorption spectra of both compounds, which are almost superimposable.

Comparison of the ^{1}H NMR spectra of the thorium and uranium complexes shows that whereas in the first case two signals for the methyl-3 and methyl-5 protons of the 3,5-dimethylpyrazole ligand are observed, in the uranium complex only one is seen. However, on lowering the temperature this signal broadens and gives rise to two non-equivalent signals in a 1:1 intensity ratio at −1.09 and 2.51 ppm in the limiting spectrum (210 °C). The proton of the N–H group also shows fluxional behaviour and on lowering the temperature the resonance broadens, collapses and narrows again. In this case, the temperature dependence of the chemical shift shows a Curie–Weiss behaviour with very different slopes above and below the coalescence temperature. Such a dynamic process has already been observed for the complex $RhCl(CO)_2(3,5\text{-}Me_2pzH)$ [4] and may involve an intramolecular exchange of the hydrogen and the metal between the two nitrogen atoms of the $3,5\text{-}Me_2pzH$ ligand.

TABLE I. Analytical and Physical Data

Complex	Analysis (%)[a]			IR (cm^{-1})			Electronic spectrum[b, c] (nm)
	C	H	N	ν(B–H)	ν(M–Cl)	ν(N–H)	
$ThCl_3[HB(3,5\text{-}Me_2pz)_3](3,5\text{-}Me_2pzH)$	33.1	4.4	14.4	2554	250	3325	
	(33.3)	(4.2)	(15.6)				
$UCl_3[HB(3,5\text{-}Me_2pz)_3](3,5\text{-}Me_2pzH)$	32.8	4.2	14.9	2555	250	3325	661(80), 667(80), 674(80), 686(110), 1071(20), 1165(80), 1221(25), 1552(30, br)
	(32.6)	(4.1)	(15.2)				
$UCl_2[HB(3,5\text{-}Me_2pz)_3](3,5\text{-}Me_2pz)$	34.1	4.2	15.9	2545	270		632(20), 660(sh), 673(sh), 680(74), 1062(31), 1138(sh), 1151(60), 1162(sh), 1205(sh)
	(34.2)	(4.1)	(16.0)				

[a] Calc. values are in parentheses. [b] In thf. [c] Extinction coefficients are in parentheses.

TABLE II. Room Temperature ^{1}H NMR Data[a]

Complex	$HB(3,5\text{-}Me_2pz)_3$		Other resonances
	(3,5-Mepz)	H(4)	
$ThCl_3[HB(3,5\text{-}Me_2pz)_3](3,5\text{-}Me_2pzH)$[b]	2.00(9H), 2.84(9H)	5.43(3H)	2.40(3H, 3,5-MepzH), 1.90(3H, 3,5-MepzH), 5.53(1H, 4-H pzH), 12.29(1H, N–H)
$UCl_3[HB(3,5\text{-}Me_2pz)_3](3,5\text{-}Me_2pzH)$[c]	−3.02(9H), 1.86(9H)	8.08(3H)	−0.69(6H, 3,5-MepzH), 6.61(1H, 4-H pzH), −7.06(1H, N–H)
$UCl_2[HB(3,5\text{-}Me_2pz)_3](3,5\text{-}Me_2pz)$[c]	−18.40(6H), −1.11(6H)	−2.50(2H)	11.16(6H, 3,5-Mepz), 37.03(1H, 4-H pz)
	13.40(3H), 13.95(3H)	28.00(1H)	

[a] The shifts are in ppm from tms; downfield shifts are positive; temperature = 300 K. [b] In benzene-d_6. [c] In chloroform-d_1.

This increased lability of the 3,5-dimethylpyrazole molecule in the uranium case can be compared with previous observations for the complexes $MCl_3[HB(3,5\text{-}Me_2pz)_3](thf)$. Whereas in the thorium case the thf molecule could not be removed, in the uranium complex it was readily lost either by prolonged pumping in vacuum or by recrystallization from a CH_2Cl_2 solution.

$UCl_2[HB(3,5\text{-}Me_2pz)_3](3,5\text{-}Me_2pz)$

From the reaction between $UCl_3[HB(3,5\text{-}Me_2pz)_3](thf)$ and one equivalent of sodium dimethylpyrazolide, the complex $UCl_2[HB(3,5\text{-}Me_2pz)_3](3,5\text{-}Me_2pz)$ can be readily isolated. The ^1H NMR spectrum of this compound indicates that only two of the three pyrazolyl rings of the $HB(3,5\text{-}Me_2pz)$ moieties are equivalent. This 2:1 pattern has always been observed when one of the Cl ligands of the trichloro complex is replaced by another ligand [5]. The dimethylpyrazolide ion shows only one resonance for the two methyl groups. All the resonances follow an approximate Curie–Weiss relationship from 300 to 210 K, indicating that the dimethylpyrazolide ligand is η^2 coordinated to the uranium centre, as observed before for the pyrazolide ion in $Cp_3U(C_3H_3N_2)$ (Cp = cyclopentadienide) [6].

The electronic spectrum of this compound was superimposable on the spectrum of a solution obtained after reaction of UCl_4 with two equivalents of $KHB(3,5\text{-}Me_2pz)_3$. Work-up of the crude product obtained from this reaction also allowed the isolation of $UCl_2[HB(3,5\text{-}Me_2pz)_3](3,5\text{-}Me_2pz)$ in a pure form. The existence of this compound in the mixture indicates that the dimethylpyrazolide ion is formed by cleavage of the ligand, but other fragments, certainly present in lesser amounts, could not be identified.

References

1 R. G. Ball, F. Edelmann, J. G. Matisons, J. Takats, N. Marques, J. Marçalo, A. Pires de Matos and K. W. Bagnall, *Inorg. Chim. Acta, 132,* 137 (1987).

2 N. Marques, A. Pires de Matos and K. W. Bagnall, *Inorg. Chim. Acta, 95,* 75 (1984).

3 D. C. Bradley, M. B. Hursthouse, J. Newton and N. P. C. Walker, *J. Chem. Soc., Chem. Commun.,* 188 (1984).

4 N. F. Borkett and M. I. Bruce, *J. Organomet. Chem., 65* C51 (1974).

5 J. Marçalo, Noémia Marques, A. Pires de Matos and K. W. Bagnall, *J. Less-Common Met., 122,* 219 (1986).

6 C. W. Eigenbrot and K. N. Raymond, *Inorg. Chem., 20,* 1553 (1981).