Uranium-sulfilimine chemistry. Hydrolysis of Cp*$_2$UCl$_2$ with HNSPh$_2$ · H$_2$O and the crystal structure of Cp*$_2$UCl(OH)(HNSPh$_2$), a metallocene terminal hydroxy complex of tetravalent uranium

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Abstract

The reaction of Cp*$_2$UCl$_2$(HNSPh$_2$) with HNSPh$_2$ · H$_2$O in 1:1 stoichiometry, produces Cp*$_2$UCl(OH)(HNSPh$_2$) in good yield. This is the first structurally characterized metallocene f-element complex containing a terminal hydroxy ligand. Cp*$_2$UCl(OH)(HNSPh$_2$) is an intermediate in the formation of a tetra uranium-oxo-cluster [Cp*(Cl)(HNSPh$_2$)U(μ_3-O)(μ_2-O)$_2$U(Cl)(HNSPh$_2$)$_2$]$_2$, which forms by hydrolysis of Cp*$_2$UCl$_2$ with excess HNSPh$_2$ · H$_2$O.
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1. Introduction

Organometallic f-block hydroxide complexes are rare. A few actinide metallocene hydroxides have been reported [1,2] and there are a few lanthanide analogues [3–11]. For the actinindes several closely related, but not formally organometallic, molecular complexes have been structurally characterized [12,13]. The preparation of f-element hydroxides generally involves controlled hydrolysis of a suitable metal precursor. For example, Andersen and co-workers synthesized the bridging hydroxide Cp″$_4$U$_2$(OH)$_2$ by treating Cp″$_3$U, Cp″ = 1,3-(Me$_3$Si)$_2$C$_5$H$_3$ or 1,3-(t-Bu)$_2$C$_5$H$_3$, with one equivalent of water [1]. When we attempted to prepare a metallocene hydroxo complex by the reaction of Cp*$_2$UCl$_2$, Cp* = C$_5$Me$_5$, with H$_2$O, we obtained a heterogeneous product that could not be characterized. In a previous paper we reported that the reaction of Cp*$_2$ UCl$_2$(HNSPh$_2$) with excess HNSPh$_2$ · H$_2$O, a reagent which supplies controlled amounts of water and absorbs hydrogen chloride generated during hydrolysis, forms a tetra-uranium-oxo cluster [Cp*(Cl)(HNSPh$_2$)U(μ_3-O)(μ_2-O)$_2$U(Cl)(HNSPh$_2$)$_2$]$_2$ [14]. During the formation of this cluster an intermediate with a NMR Cp* resonance at about −2.7 ppm, appears and disappears [15]. We have now identified this intermediate as Cp*$_2$ UCl(OH)(HNSPh$_2$), which is the first structurally characterized metallocene f-element complex containing a terminal hydroxy ligand.

2. Experimental

2.1. General remarks

All reactions were carried out under a dinitrogen atmosphere using normal Schlenk, glove box and vacuum techniques. Solvents were dried and deoxygenated over

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sodium-benzophenone and were distilled prior to use. $Cp*_2UCl_2$ was prepared using a literature method [16] and $HNSPh_2 \cdot H_2O$ was purchased from Aldrich chemical company. $Cp*_2UCl_2(HNSPh_2)$ was synthesized by the reaction of $Cp*_2UCl_2$ with anhydrous $HNSPh_2$ [14]. ^1H NMR spectra were obtained using a Nicolet QE 300 MHz spectrometer and samples were prepared in d_6-benzene, d_8-toluene or d_8-tetrahydrofuran. IR spectra were recorded on a Perkin Elmer 1430 spectrometer or a Nicolet-740 IR spectrometer operating in the Fourier transform mode.

2.2. Synthesis of Cp*_2UCl(OH)(HNSPh_2)

In a glove box, a solution of 73 mg (0.33 mmol) of $HNSPh_2 \cdot H_2O$ in 10 ml of benzene was slowly added to a solution of 193 mg (0.33 mmol) of $Cp*_2 UCl_2(HNSPh_2)$ in 15 ml of benzene. The sample turned light green from dark orange and a white precipitate began to form. After 3 h the solution was filtered through a medium porosity frit and evaporated to dryness. The green oily residue was dried under vacuum overnight, dissolved in 3 ml of benzene and stored at room temperature for a week during which period green crystals formed. These crystals were separated from the solution by filtration, rinsed with 2 ml of pentane and dried under vacuum to yield 120 mg (63.7%) of $Cp*_2UCl(OH)(HNSPh_2)$. ^1H NMR (d8-thf) *at 23 °C*: −2.7 ppm (s, 30H, Cp*), −10.5 ppm (br), −0.5 (br), −163 ppm (br); *at −60 °C*: −4.1 ppm (Cp*, 30H), −2.0 ppm, −0.5 ppm, −15.1 ppm, −163 ppm (br), 7.2 (br), 7.4 (br), 9.2 (br). IR (cm^{-1}): 3290 (w), 3150 (br), 3050 (s), 2900 (m), 2870 (m), 2250 (m), 1950 (s), 1875 (s), 1810 (s), 1560 (s), 1455 (m), 1440 (s), 1350 (w), 1250 (w), 1150 (m), 1075 (m), 1020 (w), 990 (w), 915 (w), 810 (m), 745 (s), 690 (s) cm^{-1}.

$Cp*_2UCl(OH)(HNSPh_2)$ decomposes in solution over several days (Section 3) and more slowly at room temperature in the solid phase. As a consequence of its instability we were unable to obtain a satisfactory elemental analysis.

2.3. Data collection and reduction of X-ray data

Single crystals of $Cp*_2UCl(OH)(HNSPh_2)$ were selected, mounted and sealed in thin-walled glass capillaries under dinitrogen. A Nicolet R3 computer-controlled diffractometer with graphite-monochromated Mo Kα radiation ($K\alpha_1 = 0.70930$ Å, $K\alpha_2 = 0.71359$ Å) and a scintillation detector with pulse height analyzer were used for the measurement of diffraction intensities. During data collection, the intensities of three standard reflections were re-measured every 97 reflections in the data set. Data manipulation, structure solution and refinement were carried out using SHELXL 97_2 Program System [17]. Data were corrected for Lorentz and

polarization effects and for decay of the intensities of check reflections during data collection and an empirical absorption correction was applied. The position of the uranium was determined by direct methods and the remaining atoms were located in subsequent rounds of difference Fourier maps and least squares refinements. All non-hydrogen atoms were refined anisotropically with restraints applied to non-U atoms. After an empirical absorption correction, the H atoms were added at calculated positions to the Cp* methyl groups, phenyl groups and the two benzene solvate molecules. The final refinement yielded R values, $R_1 = 6.51\%$, $wR_2 = 16.30\%$ ($I > 2\sigma(I)$ and $R = 9.81\%$, $wR_2 = 18.45\%$ (all data)).

Crystalline $Cp*_2UCl(OH)(HNSPh_2)$ belongs to the monoclinic space group $P2(1)/c$. There are two nearly identical $Cp*_2UCl(OH)(HNSPh_2)$ molecules and two benzene molecules in the asymmetric unit leading to eight molecules of $Cp*_2UCl(OH)(HNSPh_2)$ and eight benzene molecules in the unit cell. Least squares plane calculations performed on the two benzene molecules in the asymmetric unit with respect to the neighboring phenyl groups indicate that these two benzenes are symmetrically non-equivalent. The crystal, data collection and refinement information are summarized in Table 1 and important bond lengths and bond angles in Table 2. A perspective drawing of $Cp*_2UCl(OH)$ $(HNSPh_2)$ is shown in Fig. 1.

Table 1
Crystallographic data for $Cp*_2UCl(OH)(HNSPh_2)$

Identification code	Hydp2
Empirical formula	C38 H48 Cl N O S U
Formula weight	840.35
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, $P(2)1/c$
Unit cell dimensions	
a (Å)	14.503(5)
b (Å)	30.095(11)
c (Å)	17.048(9)
α (°)	90
β (°)	102.20(3)
γ (°)	90
Volume	7273(5) Å^3
Z, Calculated density (Mg/m^3)	8, 1.531
Absorption coefficient (mm^{-1})	4.623
$F(000)$	3312
Crystal size (mm)	$1.0 \times 0.5 \times 0.5$
θ Range for data collection	1.59° to 22.56°
Limiting indices	$-15 \leqslant h \leqslant 15$, $-6 \leqslant k \leqslant 32$, $-2 \leqslant 1 \leqslant 18$
Reflections collected/unique	10095/9343 [R(int) = 0.0511]
Completeness to theta = 22.56	97.5%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9343/812/799
Goodness-of-fit on F^2	1.077
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0651$, $wR_2 = 0.1630$
R indices (all data)	$R_1 = 0.0981$, $wR_2 = 0.1845$
Largest differential peak and hole (e Å^{-3})	2.079 and −2.474

Table 2
Selected bond lengths (Å) and angles (°) for Cp*$_2$UCl(OH)(HNSPh)$_2$

Molecule 1			
U(1)–O(1)	2.117(9)	U(1)–C(11)	2.77(1)
U(1)–N(1)	2.47(2)	U(1)–C(12)	2.81(2)
U(1)–Cl(1)	2.746(4)	U(1)–C(13)	2.79(2)
N(1)–S(1)	1.57(1)	U(1)–C(14)	2.75(1)
S(1)–C(51)	1.81(2)	U(1)–C(15)	2.79(1)
S(1)–C(61)	1.77(2)		
U(1)–N(1)–S(1)	128.4(7)	N(1)–S(1)–C(61)	107.7(7)
Cl(1)–U(1)–O(1)	147.0(7)	C(51)–S(1)–C(61)	98.1(7)
N(1)–S(1)–C(51)	110.2(7)		
Molecule 2			
U(2)–O(2)	2.117(9)	U(2)–C(31)	2.73(1)
U(2)–N(2)	2.47(1)	U(2)–C(32)	2.76(1)
U(2)–Cl(2)	2.757(4)	U(2)–C(33)	2.80(1)
N(2)–S(2)	1.57(1)	U(2)–C(34)	2.80(1)
S(2)–C(71)	1.78(2)	U(2)–C(35)	2.77(1)
S(2)–C(81)	1.83(2)		
U(2)–N(2)–S(2)	128.9(6)	N(2)–S(2)–C(71)	109.1(7)
Cl(2)–U(2)–O(2)	147.4(3)	C(71)–S(2)–C(81)	97.9(7)
N(2)–S(2)–C(81)	109.8(7)		
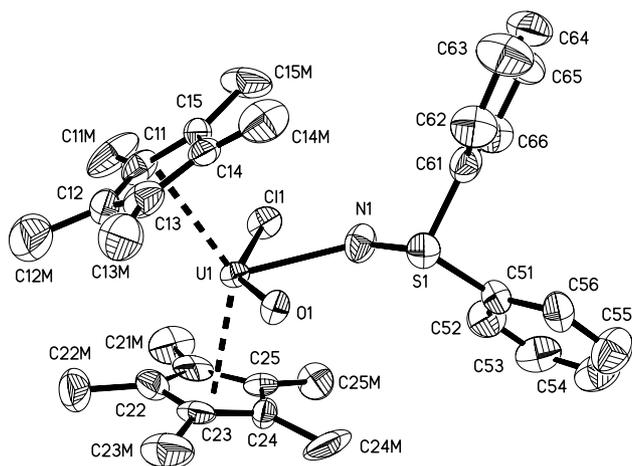
Fig. 1. Ortep diagram of the non-hydrogen atoms of Cp*$_2$UCl(OH)(HNSPh)$_2$ showing the atom labeling scheme.

3. Results and discussion

The reaction of Cp*$_2$UCl$_2$(HNSPh$_2$) with HNSPh$_2$ · H$_2$O produces Cp*$_2$UCl(OH)(HNSPh$_2$), which is a green crystalline compound. The heavy atom structure of Cp*$_2$UCl(OH)(HNSPh$_2$) is very similar to Cp*$_2$UCl$_2$(HNSPh$_2$) [18] with the former being derived from the latter by the substitution of a hydroxide for a chloride. The bond distances and angles within the Cp*$_2$U and U–N(H)SPh$_2$ moieties are unremarkable and lie in the same range as those in Cp*$_2$UCl$_2$(HNSPh$_2$), Cp*$_2$UCl$_2$ (HNPPh$_3$) and [Cp*(Cl)(HNSPh$_2$)U(μ$_3$-O)(μ$_2$-O)$_2$U(Cl) (HNSPh$_2$)$_2$]$_2$ [14,18]. Placing the imino hydrogen at its calculated position, it is directed towards the chloride.

The N---Cl separations of about 3.0 Å are within the range for N–H---Cl hydrogen bonds [19]. This geometry resembles that in Cp*$_2$UCl$_2$(HNPPh$_3$), Cp*$_2$UCl$_2$ (HNSPh$_2$) and [Cp*(Cl)(HNSPh$_2$)U(μ$_3$-O)(μ$_2$-O)$_2$U(Cl) (HNSPh$_2$)$_2$]$_2$ where N–H---Cl hydrogen bonding is proposed [14,18].

The most interesting structural question involves the assignment of the oxygen bonded to the uranium as an OH group. Based on an analysis of data in the Cambridge Crystallographic Database [20], typical U=O distances are less than 1.95 Å, terminal U–OH should be about 2.1 Å, and U–OH$_2$ should exceed 2.3 Å. Some comparisons include [U(tpa)$_2$(OH)$_2$]$^{2+}$, tpa = tris[(2-pyridyl)methyl]amine, with U–O distances 2.127(1) Å and 2.147(1) Å [12]; HO–U(NN′$_3$)(CH$_2$PMe$_3$), NN′$_3$= CH$_2$CH$_2$NSiMe$_2$Bu^t, whose U–O distance is 2.145(6) Å [13]; H$_2$O–UCp*$_2$(Otf)$_2$, Otf = trifluoromethanesulfonate, with a U–O distance to the coordinated water molecule of 2.57 Å [21]; and Cp*$_2$U(O-2,6-^{i}Pr-C$_6$H$_3$)(O), which is a U(V) complex with a terminal O–U distance of 1.859(6) Å and a U–O(-2,6-^{i}Pr-C$_6$H$_3$) separation of 2.135 (5) Å [22]. Clearly, the 2.117 (9) Å U–O bond in Cp*$_2$UCl(OH)(HNSPh$_2$) falls in the range expected for a hydroxide. It is too long for a terminal oxo, and too short for a coordinated water molecule. Additionally, the intermolecular distances O(1)–Cl(2), 3.25 Å, and O(2)–Cl(1), 3.32 Å, respectively, lie in the range observed for O–H---Cl hydrogen bonding, which also supports the assignment of the ligand as hydroxide [19]. The U(2)–O(2)–Cl(1), 150.4°, and U(1)–O(1)–Cl(2), 152.5°, angles are consistent with a large U–O–H angle, which would be expected if the U–O bond possesses significant pi character.

Based on the structural evidence presented, the reaction of Cp*$_2$UCl$_2$(HNSPh$_2$) with HNSPh$_2$ · H$_2$O is

Cp*$_2$UCl$_2$(HNSPh$_2$) + HNSPh$_2$ · H$_2$O

$\rightarrow$ Cp*$_2$UCl(OH)(HNSPh$_2$) + [H$_2$NSPh$_2$]Cl
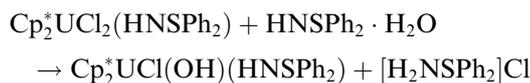
In this reaction, HNSPh$_2$ · H$_2$O is the source of a controlled amount of water and absorbs HCl as it is generated during hydrolysis. The ^{1}H NMR spectrum of freshly prepared Cp*$_2$UCl(OH)(HNSPh$_2$) dissolved in deuterated THF contains a sharp signal at −2.7 ppm; this can be assigned to the Cp* protons on the basis of relative intensity. In addition, broad signals appear at −0.5, −10.5, and −163 ppm. Upon cooling these peaks sharpen considerably. By −60 °C the former two are resolved into three resonances at −0.5, −2.0 and −15.1 ppm that can be assigned to the aromatic protons on the phenyl groups. The resonance at −163 ppm is assigned to the N–H proton by analogy to the value of −142 ppm observed in Cp*$_2$UCl$_2$(HNSPh$_2$) [18]. Based on this assignment, the O–H proton resonance was not located. However, exchange between the hydroxy and imino protons was not eliminated.

In solution $Cp^*_2UCl(OH)(HNSPh_2)$ decomposes over several days. NMR spectra monitored periodically show that the amount of $Cp^*_2UCl(OH)(HNSPh_2)$ decreases and peaks characteristic of $Cp^*_2UCl_2(HNSPh_2)$, Cp^*H, and $HNSPh_2$ grow in. In addition, $[Cp^*(Cl)(HNSPh_2)U(\mu_3\text{-}O)(\mu_2\text{-}O)_2U(Cl)(HNSPh_2)_2]_2$ precipitates [14]. Apparently, upon coordination to uranium, the hydroxyl group becomes acidic enough to hydrolyze moisture sensitive species. This may explain why organouranium-hydroxy complexes are often difficult to obtain in a state of high purity and in good yield.

4. Supporting material

Crystallographic data (excluding structural factors) for the structural analysis of $Cp^*_2UCl(OH)(HNSPh_2)$ have been deposited with the Cambridge Crystallographic Data Centre, CCDC 227353. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

References

[1] W.W. Lukens Jr., S.M. Beshouri, L.L. Blosch, R.A. Andersen, J. Am. Chem. Soc. 118 (1996) 901.

[2] J. Berthet, M. Ephritikhine, M. Lance, M. Nierlich, J.J. Vigner, Organomet. Chem. 460 (1993) 47.

[3] G. Lin, W. Wong, Polyhedron 14 (1995) 3167.

[4] I.P. Beletskaya, A.Z. Voskoboynikov, E.B. Chuklanova, N.I. Kirillova, A.K. Shestakova, I.N. Parshina, A.I. Gusev, G.K.I. Magomedov, J. Am. Chem. Soc. 115 (1993) 3156.

[5] D. Deng, Y. Jiang, C. Qian, G. Wu, P.J. Zheng, J. Organomet. Chem. 470 (1994) 99.

[6] W.A. Hermann, R. Anwander, M. Kleine, K. Oefele, J. Riede, W. Scherer, Chem. Ber. 125 (1992) 2391.

[7] Z. Xie, Z. Liu, K. Chui, F. Xue, T.C.W.J. Mak, J. Organomet. Chem. 588 (1999) 78.

[8] P.B. Hitchcock, M.F. Lappert, S. Prashar, J. Organomet. Chem. 413 (1991) 79.

[9] D. Deng, F. Song, Z. Wang, C. Qian, G. Wu, P. Zheng, Polyhedron 11 (1992) 2883.

[10] H. Schumann, J.L. Loebel, J. Pickardt, C. Qian, Z. Xie, Organometallics 10 (1991) 215.

[11] H. Schumann, M.R. Keitsch, J. Demtschuk, G.A. Molander, J. Organomet. Chem. 582 (1999) 70.

[12] L. Karmazin, M. Mazzanti, J. Pécaut, Inorg. Chem. 42 (2003) 5900.

[13] P. Roussel, R. Boaretto, A.J. Kingsley, N.W. Alcock, P. Scott, J. Chem. Soc. Dalton Trans. (2002) 1423.

[14] R.E. Cramer, K.A.N.S. Ariyaratne, J.W. Gilje, Z. Anorg. Allg. Chem. 621 (1995) 1856.

[15] K.A.N.S. Ariyaratne, Ph.D. Dissertation, University of Hawaii, 1992.

[16] P.J. Fagan, J.M. Manriquez, E.A. Maata, A.N. Seyam, T.J. Marks, J. Am. Chem. Soc. 103 (1981) 6650.

[17] Crystal Structure Refinement-SHELXTL Ver 6.10 W95/98/NT/ 2000. Copyright © 2000 Bruker – AXS.

[18] R.E. Cramer, S. Roth, J.W. Gilje, Organometallics 8 (1981) 2327.

[19] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, Pergamon Press Ltd, England, 1984, p. 65.

[20] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, J. Chem. Soc. Dalton Trans. (1989) S1.

[21] J.C. Berthet, M. Lance, M. Nierlich, M. Ephritikhine, Chem. Commun. (1998) 1373.

[22] D.S.J. Arney, C.J. Burns, J. Am. Chem. Soc. 115 (1993) 9840.