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URANIUM - SULFILIMINE CHEMISTRY : THE PREPARATION AND CHARACTERIZATION OF $Cp^*_2UCl(NSPh_2)$

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ABSTRACT

The reaction of $Cp^*_2UCl_2$ with $LiNSPh_2$ in 1:1 ratio, produces $Cp^*_2UCl(NSPh_2)$ in high yield. $[NSPh_2]^-$ ligand replaces the phosphoylide ligand $[CHP(Me)Ph_2]^-$ from $Cp^*_2UCl(CH_2)_2PPh_2$ when treated with $HNSPh_2$ in 1:1 ratio forming $Cp^*_2UCl(NSPh_2)$. $Cp^*_2UCl(NSPh_2)$ has been characterized by usual chemical and physical methods and by single crystal X-ray diffraction. $Cp^*_2UCl(NSPh_2)$ is the first structurally characterized f-element sulfilimide complex. (Cp* = pentamethylcyclopentadienyl, Ph = phenyl)

1. INTRODUCTION

Imido ligands, NR^{2-}, can donate upto three electron pairs upon coordination to a metal. Although many transition metal imide complexes are known[1], f-element imide complexes are relatively rare[2]. As the structure of the phosphine imide complex Cp_3UNPPh_3 suggested a U-N triple bond[3], the coordination chemistry of electronically similar sulfilimide $[NSR_2]^-$ ligands were also expected to show similar chemistry with uranium.

The ligand properties of sulfilimines and sulfilimides have received scant attentiom. A recent paper discussed the preparation and structures of sulfilimine complexes $Cp^*_2UCl_2(HNSPh_2)$ and $[Cp^*(Cl)(HNSPh_2)U(\mu_3\text{-}O)(\mu_2\text{-}O)_2U(Cl)(HNSPh_2)_2]_2$[4]. They are the only $HNSPh_2$ complexes reported to date. While structurally characterized sulfilimide complexes of f-block elements are currently unknown, a few well characterized transition metal sulfilimide complexes have been reported[5]. The organoactinide chemistry of the ligands $[CHPR_3]^-$ and $[NPR_3]^-$ has been well established[3]. The sulfilimide ligand $[NSR_2]^-$ which is electronically similar to the above ligands also show similar behaviour with early actinides. This paper describes the successful preparation and the crystal structure of $Cp^*_2UCl(NSPh_2)$, the first well characterized f-element sulfilimide complex.

2. EXPERIMENTAL

All reactions were carried out under a dry nitrogen atmosphere using normal Schlenk, glove box and vacuum line techniques. Solvents were dried and deoxygenated over sodium-benzophenone and were distilled prior to use. $Cp^*_2UCl_2$ was prepared using literature methods[6] and $HNSPh_2$ was purchased from Aldrich chemical company as $HNSPh_2.H_2O$ and dehydrated under high vacuum for three days at room temperature. NMR spectra were obtained using a Nicolet QE 300 MHz spectrometer and samples were prepared in d_6-benzene, d_8-tetrahydrofuran, d_3-acetonitrile and/or d_8-toluene. IR spectra were recorded on a Perkin Elmer1430 spectrometer or a Nicolet-740 IR spectrometer operating in the Fourier transform mode.

Preparation of $LiNSPh_2$

8 ml of 0.6 M n-butyl lithium was added slowly to a solution of 400 mg (2.0 mmole) of $HNSPh_2$ in 25 ml of tetrahydrofuran under nitrogen at room temperature. The yellow solution was stirred at room temperature for 15 mins and evaporated to dryness. The yellow crystalline $LiNSPh_2$ was washed with 2 ml of pentane and desolvated in high vacuum for three days.

Preparation of $Cp^*_2UCl(NSPh_2)$

(i) A solution of 84 mg (0.40 mmole) of $LiNSPh_2$ in 25 ml of toluene was added slowly to 230 mg (0.40 mmole) of $Cp^*_2UCl_2$ dissolved in 25 ml of toluene and held at -78°C. The solution was allowed to warm slowly to room temperature for a period of six hours. The dark red solution was filtered through a medium porosity frit and reduced in volume to about 5 ml. Approximately 3 ml of pentane was added and the solution was stirred at room temperature for three days during which a dark red-black microcrystalline material formed in the flask. The solid was filtered, rinsed with 0.5 ml of pentane, dried under strong vacuum and to yield 127 mg (72 %) of dark red $Cp^*_2UCl(NSPh_2)$. ^{1}H-NMR (d_8-toluene): 2.27 ppm (s, 30 H, Cp^*), 8.37 ppm (t, 2H, J = 7 Hz, p-C_6H_5), 8.48 ppm (t, 4H, J = 7 Hz, m-C_6H_5), 14.12 ppm (d, 4 H, J = 7 Hz, o-C_6H_5), IR : 3010 vs, 300 w, 2975 vs, 2820 s, 2690 w, 1555 m, 1475 s, 1450 w, 1360 s, 1270 vs, 1025 vs, 1000 s, 800 vs, 750 s, 695 s cm^{-1}. Successful results could not be obtained from elemental analysis as traces of solvent were present in the sample. Reproducible mass spectra could not be obtained due to low volatility of the compound.

(ii) A solution of 80 mg (0.40 mmole) of $HNSPh_2$ dissolved in 25 ml of toluene was added slowly to a solution of 304 mg (0.40 mmole) of $Cp^*_2UCl(CH_2)_2PPh_2$ in 25 ml of toluene. After stirring for 3 hrs at room temperature the dark red solution was filtered through a medium porosity frit and evaporated to dryness to obtain a dark red powder. This was rinsed with 2 ml of pentane and dried under vacuum to yield 193 mg (64 %) of dark red powder.

Collection and reduction of X-ray data

Single crystals of $Cp^*_2UCl(NSPh_2)$ were mounted and sealed in thin walled capillaries under dinitrogen. A Nicolet R3 computer controlled diffractometer with graphite monochromatised MoK_α radiation ($K\alpha_1$ = 0.70930 A, $K\alpha_2$ = 0.71359 A) and a scintillation detector with pulse height analyser was used for the measurement of diffraction intensities. During data collection the intensities of three standard reflections were re-measured every 97 reflections. Data manipulation, structure solution and refinement were carried out using the SHELXTL PLUS Program System. Data were corrected for Lorentz and polarization effects and for decay of the intensities of check reflections during data collection. An empirical absorption correction was applied to each data set.

The structure of $Cp^*_2UCl(NSPh_2)$ was solved in the monoclinic space group p2 1/n. The position of the uranium was determined by Patterson methods and the remaining atoms were located from a series of difference Fourier maps and least squares refinements. No hydrogens were located nor were included at calculated positions. All atoms were refined anisotropically except ring carbons of the phenyl groups which were refined isotropically as rigid bodies. A pentane molecule lying on a center of inversion, was also observed in the crystal structure. Refinement converged to R = 6.55 % and R_g = 8.00 %.

3. RESULTS AND DISCUSSION

Reactions and interpretation of spectral data

Attempts to synthesize organouranium derivatives of $[NSPh_2]^-$ ligand by the dehydrochlorination of $Cp^*_2UCl_2(HNSPh_2)$ and the treatment of $Me_3SiNSPh_2$ with $Cp^*_2UCl_2$ were unsuccessful. However, when $Cp^*_2UCl_2$ is treated with $LiNSPh_2$ in a 1:1 molar ratio, a dark red complex forms according to the following equation.

$Cp^*{}_2UCl_2 + LiNSPh_2 \dashrightarrow Cp^*{}_2UCl(NSPh_2) + LiCl$ (1)

Alternatively, $Cp^*{}_2UCl(NSPh_2)$ can be synthesized by reacting $HNSPh_2$ with $Cp^*{}_2UCl(CH_2)_2PPh_2$, as shown below.

$Cp^*{}_2UCl(CH_2)_2PPh_2 + HNSPh_2 \dashrightarrow Cp^*{}_2UCl(NSPh_2) + CH_2{=}P(CH_3)Ph_2$ (2)

The phosphoylide ligand which is a strong base abstracts the imino hydrogen of $HNSPh_2$ and is replaced by the sulfilimide ligand in this reaction.

$Cp^*{}_2UCl(NSPh_2)$ is stable for long periods of time when stored under anaerobic anhydrous conditions but decomposes rapidly when exposed to moisture or oxygen. $Cp^*{}_2UCl(NSPh_2)$ was characterized by infrared and ^{1}H-NMR spectroscopy and by single crystal X-ray diffraction. The infrared spectrum contains strong absorption bands for the C-H stretches of the phenyl and Cp* groups in the range 2975 - 3010 cm^{-1} where as a strong N-S stretch occurs near 800 cm^{-1}. Furthermore, intense bands occur at 1555 cm^{-1} and 1450 cm^{-1} for the C=C(Ph) and S-C(Ph) bonds respectively. These assignments are in agreement with those of known metal-sulfilimide complexes[5]. The ^{1}H-NMR spectrum exhibits large chemical shifts typical of paramagnetic U(IV) complexes[3,4] and contains signals for the phenyl and Cp* groups. While a sharp singlet occurs at 2.27 ppm for the Cp* protons, the phenyl groups form a doublet at 14.12 ppm for the ortho protons and triplets at 8.37 and 8.48 ppm respectively for the meta and para protons.

X-ray structural studies

A perspective drawing of $Cp^*{}_2UCl(NSPh_2)$ is shown in fig. 1 and the crystal data are summarized in Table 1. The positional and thermal parameters are listed in Tables 2, 3 and 4 while the bond lengths and angles are given in Table 5.

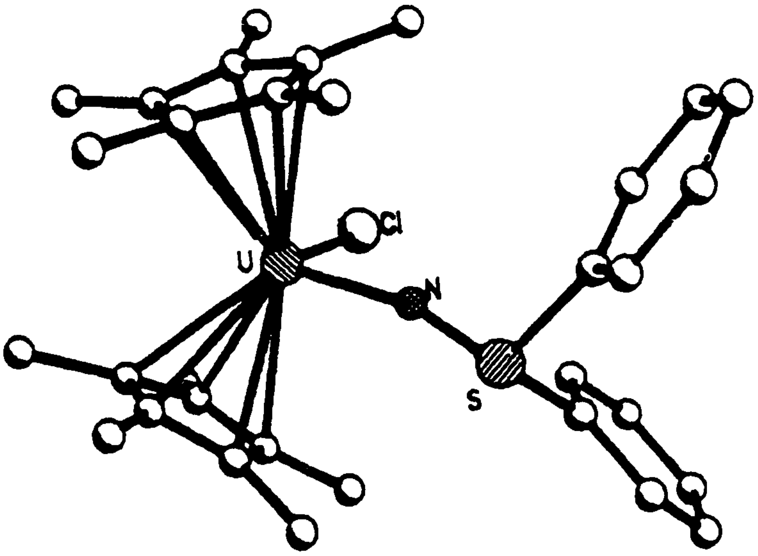


Fig. 1. The Molecular Structure of $Cp^*{}_2UCl(NSPh_2)$

The structure is of Cp_2ML_2 type and belongs to the bent metallocene family. It clearly demonstrates nitrogen coordination to uranium. The ring centroid-U-ring centroid angle 134° and the average U-C(Cp*) distance 2.73(5) A are within the ranges found for other actinide complexes[7]. The U-N-S angle of 164.4(9)°, is consistent with a sp hybridized nitrogen atom. This angle is significantly wider than that in $Cp^*{}_2UCl_2(HNSPh_2)$ 134(1)°

Table 1. Summary of Crystal Data for $Cp^*_2UCl(NSPh_2)$

Formula	$Cp^*_2UCl(NSPh_2)_2.1/2\ C_5H_{12}$	D(cacd), Mg/M^3	1.504
Formula Weight	780.3	μ_{calc}, mm^{-1}	4.625
crystal dim.(mm)	0.5 x 0.1 x 1.0	abs. corr.range	0.106-0.058
crystal system	monoclinic	rad.(Mo, Kα), A	0.71013
space group	p2 1/n	scan rate,° min^{-1}	1.5-15.0
a, A	12.120(5)	scan type	omega
b, A	13.249(6)	total obs.	3673
c, A	21.6444(8)	unique obs.	3149
β,°	95.57(3)	unique data with	
V, A^3	3445(2)	F>2.0 σ(F)	2530
Z	4	no. of parameter	267
crystal shape	rectangular prism	overdeter. ratio	9.5
crystal color	reddish black	R	0.0655
Rg	0.0800		

$$R = \Sigma(|F_o - F_c|) / \Sigma(F_o)$$
$$R_g = [\Sigma(|F_o - F_c|^2) / \Sigma(F_o^2)]^{1/2}$$

Table 2. Positional parameters of anisotropically refined atoms for $Cp^*_2UCl(NSPh_2)$

atom	x	y	z
U	0.0065(1)	0.0072(1)	0.2193(1)
N	-0.140(1)	-0.045(1)	0.1664(7)
S	-0.2632(4)	-0.0731	0.1430(2)
Cl	0.0503(5)	0.1473(3)	0.1414(3)
C(11)	0.210(2)	-0.60(2)	0.192(2)
C(12)	0.205(3)	-0.90(3)	0.254(2)
C(13)	0.127(3)	-0.161(2)	0.2537(2)
C(14)	0.083(2)	-0.181(2)	0.196(2)
C(15)	0.133(3)	-0.118(2)	0.158(1)
C(11M)	0.281(3)	0.007(2)	0.154(3)
C(12M)	0.298(3)	-0.037(4)	0.298(4)
C(13M)	0.123(5)	-0.216(4)	0.317(2)
C(14M)	0.000(2)	-0.265(2)	0.181(3)
C(15M)	0.105(3)	-0.125(3)	0.088(1)
C(21)	0.036(3)	0.098(5)	0.336(2)
C(22)	-0.042(4)	0.034(3)	0.337(1)
C(23)	-0.136(2)	0.062(2)	0.301(1)
C(24)	-0.110(2)	0.149(2)	0.277(9)
C(25)	-0.004(3)	0.172(2)	0.294(1)
C(21M)	0.119(3)	0.065(4)	0.392(2)
C(22M)	-0.085(4)	-0.069(3)	0.373(2)
C(23M)	-0.259(3)	0.023(3)	0.288(2)
C(24M)	-0.186(3)	0.222(3)	0.227(1)
C(25M)	0.060(6)	0.262(4)	0.289(3)
C(50)	1.000	0.500	0.000
C(51)	0.93(1)	0.44(1)	-0.003(8)
C(52)	0.921(7)	0.419(6)	0.071(4)

Table 3. Thermal parameters of anisotropically refined atoms for $Cp^*{}_2UCl(NSPh_2)$

atom	U(11)	U(22)	U(33)	U(12)	U(13)	U(23)
U	0.046(1)	0.051(1)	0.063(1)	0.008(1)	0.014(1)	-0.001(1)
N	0.047(9)	0.076(9)	0.06(1)	0.015(8)	-0.005(7)	-0.006(8)
S	0.054(3)	0.109(4)	0.058(3)	0.000(3)	0.016(3)	-0.010(3)
Cl	0.109(5)	0.083(3)	0.122(5)	0.024(3)	0.066(4)	0.035(3)
C(11)	0.02(1)	0.04(1)	0.29(5)	0.02(1)	0.05(2)	0.03(2)
C(12)	0.12(3)	0.11(3)	0.18(3)	0.09(2)	-0.05(3)	-0.04(3)
C(13)	0.16(3)	0.09(2)	0.09(2)	0.07(2)	0.04(2)	0.03(2)
C(14)	0.07(1)	0.06(1)	0.14(2)	0.02(1)	0.02(2)	-0.03(2)
C(15)	0.10(2)	0.12(2)	0.08(2)	0.05(2)	0.06(2)	0.02(2)
C(11M)	0.17(4)	0.17(3)	0.6(1)	0.04(2)	0.25(5)	0.13(4)
C(12)M	0.1093)	0.42(7)	0.8(1)	0.12(4)	-0.18(5)	-0.49(9)
C(13M)	0.7(1)	0.32(5)	0.18(4)	0.36(7)	0.24(6)	0.15(4)
C(14M)	0.104(2)	0.05(2)	0.67(8)	-0.3(2)	0.06(3)	-0.10(3)
C(15M)	0.23(4)	0.31(5)	0.10(2)	0.16(4)	0.04(2)	-0.03(3)
C(21)	0.08(2)	0.38(8)	0.10(3)	0.03(3)	-0.04(2)	-0.13(4)
C(22)	0.26(5)	0.18(3)	0.04(2)	0.17(4)	-0.00(2)	0.01(2)
C(23)	0.14(2)	0.06(1)	0.13(2)	-0.04(2)	0.11(2)	-0.07(2)
C(24)	0.09(2)	0.05(1)	0.08(1)	0.03(1)	0.01(1)	-0.02(1)
C(25)	0.16(3)	0.11(2)	0.12(2)	-0.12(2)	0.09(2)	-0.07(2)
C(21M)	0.23(4)	0.49(7)	0.18(4)	0.26(5)	-0.13(3)	-0.18(5)
C(22M)	0.40(7)	0.16(3)	0.17(4)	0.02(4)	0.17(4)	-0.00(3)
C(23M)	0.15(3)	0.26(4)	0.29(5)	-0.12(3)	0.17(3)	-0.19(4)
C(24M)	0.31(4)	0.25(4)	0.12(2)	0.24(4)	0.00(3)	-0.02(2)
C(25M)	0.8(1)	0.35(6)	0.46(7)	-0.44(7)	0.55(8)	-0.33(6)
C(50)	0.13(6)	0.291)	1.0(5)	0.02(6)	-0.1(2)	-0.2(2)
C(51)	0.4(2)	0.4(1)	0.5(2)	0.2(1)	-0.3(1)	-0.3(1)
C(52)	0.23(6)	0.23(5)	0.30(7)	0.04(4)	0.05(5)	0.02(5)

Table 4. Positional and Thermal parameters of isotropically refined atoms for $Cp^*{}_2UCl(NSPh_2)$

atom	x	y	z	u
C(31)	-0.263(1)	-0.1620(8)	0.0819(5)	0.0064(5)
C(32)	-0.318(1)	-0.2536(8)	0.0882(5)	0.0077(5)
C(33)	-0.314(1)	-0.3291(8)	0.0436(5)	0.0091(6)
C(34)	-0.256(1)	-0.3131(8)	-0.0071(5)	0.0087(6)
C(35)	-0.202(1)	-0.2215(8)	-0.0134(5)	0.0083(6)
C(36)	-0.206(1)	-0.1460(8)	0.0311(5)	0.0068(5)
C(41)	-0.326(1)	0.0302(9)	0.0987(6)	0.0093(6)
C(42)	-0.261(1)	0.1054(9)	0.0764(6)	0.0093(6)
C(43)	-0.312(1)	0.1859(9)	0.0421(6)	0.0126(9)
C(44)	-0.428(1)	0.1913(9)	0.0301(6)	0.0132(9)
C(45)	-0.493(1)	0.1161(9)	0.0525(6)	0.0133(9)
C(46)	-0.442(1)	0.0356(9)	0.0868(6)	0.0119(8)

Table. 5 Bond lengths and angles for $Cp^*{}_2UCl(NSPh_2)$ [a]Cp(1) and Cp(2) are the centroids of the rings C(11)-C(15) and C(21)-C(25) respectively.

bond distance, (A)	
U-Cl	2.609(6)
U-N	2.10(1)
N-S	1.55(1)
S-C(41)	1.78(1)
U-C(11)	2.76(3)
U-C(12)	2.75(4)
U-C(13)	2.71(3)
U-C(14)	2.73(2)
U-C(15)	2.71(3)
U-C(21)	2.77(5)
U-C(22)	2.71(3)
U-C(23)	2.73(3)
U-C(24)	2.70(2)
U-C(25)	2.73(3)
U-Cp(1)[a]	2.48
U-Cp(2)[a]	2.48

bond angle, $(^0)$	
Cl-U-N	96.4(4)
U-N-S	164.4(9)
N-S-C31	108.1(7)
C(31)-S-C(41)	98.7(6)
Cp(1)-U-Cl	103.7[a]
Cp(1)-U-N	107.0[a]
Cp(2)-U-Cl	103.9[a]
Cp(2)-U-N	106.6[a]
Cp(1)-U-Cp(2)	133.2[a]

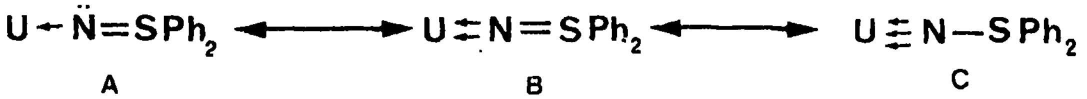
Table 6. Structural data for various sulfilimine/sulfilimide complexes

compound	**M-N, A**	**metallic radius, A**	**diff, A**	**M-N-S, ^{o}**
$F_4W(NSPh_2)_2$	1.807(4),1.851(4)	1.304	0.50, 0.55	171.7(3),138.4(3)
$Cl_2VO(NSPh_2)$	1.748(7), 1.723(7)	1.224	0.52, 0.50	134.5(4), 141.9(5)
$Cp^*{}_2UCl(NSPh_2)$	2.10(1)	1.60	0.50	164.4(9)
$Cp^*{}_2UCl_2(HNS\text{-}Ph_2)$	2.44(3)	1.60	0.89	134(1)

where the nitrogen is sp^2 hybridised. The Cl-U-N angle in $Cp^*{}_2UCl(NSPh_2)$ 96.4(4)^o, is narrower than the Cl-U-Cl angle in $Cp^*{}_2UCl_2(HNSPh_2)$ 145.9(3)^o. This indicates that the uranium atom is less sterically crowded in $Cp^*{}_2UCl(NSPh_2)$ than in $Cp^*{}_2UCl_2(HNSPh_2)$. The U-Cl bond 2.609(6) A is significantly shorter than that in $Cp^*{}_2UCl_2(HNSPh_2)$ and is normal for tetravalent uranium which ranges from 2.56 - 2.60 A[8].

The U-N bond distance 2.10(1)A in $Cp^*{}_2UCl(NSPh_2)$ is significantly shorter than that in $Cp^*{}_2UCl_2(HNSPh_2)$ and among the shortest found for $Cp^*{}_2U$-(N-donor) complexes. This distance is comparable to that in Cp_3UNPPh_3, 2.07(2) A which represents a U-N multiple bond and reflects the strong donor power of the $[NSPh_2]^-$ ligand. The U-N distance could be considered as a measure of the extent of electron donation of the ligand.

It has been shown that the metal-nitrogen triple bond is approximately 0.41 A longer than the appropriate Pauling metallic radius for a given metal complex[1a].The result from the subtraction of the estimated metallic radius of uranium (IV) 1.60 A from the U-N bond distances has been used in studying the nature of the U-N bond in uranium-phophine imide complexes[3]. The results of such calculations on various uranium-sulfilimine/sulfilimide systems are given in table 6. The 0.50 A difference in $Cp^*_2UCl(NSPh_2)$ is consistent with a U-N bond order between 2 and 3. For comparison, the corresponding values for Cp_3UNPh and Cp_3UNPPh_3 where U-N triple bonds are known to occur, are 0.47 A and 0.44 A respectively. The large U-N bond order in $Cp^*_2UCl(NSPh_2)$ could be explained by considering the following resonance forms where the true coordination mode of the ligand lies between B and C.



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