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Syntheses of New Uranium Complexes $Cl_2U(\pi\text{-}S_4N_4)$ and $(C_5H_5)_3UClAlCl_3 \cdot THF$

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Abstract

The new bridging complexes $Cp_3UClClAlCl_2$ and $Cp_3UClClAlCl_2 \cdot THF$ were synthesized by reaction of triscyclopentadienyl uranium chloride with aluminum trichloride in the presence of different solvents. The $Cp_3UClClAlCl_2 \cdot THF$ complex is proposed to have a square bipyramidal structure with THF occupying the sixth position. A new inorganic cyclooctatetraene uranium complex, $UCl_2(S_4N_4)$, was also synthesized by uranium tetrachloride with tetrasulfur tetranitride.

Introduction

Although many research studies on organoactinides have been reported, most of them concentrated on the cyclopentadienyl π-complexes. The chemistry of inorganic heterocycles as π-bonding ligands, such as cyclothiazene (S_4N_4), borazine ($B_3N_3H_6$), *nido*-7,8-$C_2B_9H_{11}^{2-}$ carborane has been less explored. The concept of aromaticity plays a prominent role in the behavior because of the polarization of the π-electron density which results in greater chemical reactivity than for the aromatic organic compound alone [1]. Raymond *et al.* have synthesized the uranium inorganic cyclopentadienyl complex $(B_9C_2H_{11})_2UCl_2$ by the reaction of *nido*-7,8-$C_2B_9H_{11}^{2-}$ with uranium tetrachloride [2]; however, the chemistry of halides as a bridge in uranium complexes has not been reported. Shehelokov *et al.* reported the bridging complex $U(COT)_2 \cdot xAlEt_2Cl$ (x is probably 2) by the reaction of uranocene with diethyl aluminum chloride [3]. The related uranium bridging complex, synthesized by Fisher and Sienel, was proposed to have oligomeric structures, consisting of pentagonal bipyramidal $U(C_5H_5)_3^+$ moieties and bridging $(CCN)_3^-$ units [4].

It is therefore of interest to investigate the new organouranium complexes.

Experimental

Apparatus and Materials

All operations were carried out in a N_2 atmosphere (glove bag or glove box) or in an evacuated system. All organic solvents were distilled and aluminum halides were sublimed before use. Triscyclopentadienyluranium chloride, uranium tetrachloride, uranium powder and tetrasulfur tetranitride were prepared according to the known methods [5–8]. Infrared spectra were obtained on Perkin-Elmer 397 and Hitachi 260-30 infrared spectrophotometers. ^{14}N, ^{27}Al and ^{1}H NMR spectra were recorded on Varian FT80A and Brucker FT-100 spectrophotometers and chemical shifts were measured relative to tetramethylsilane as internal and nitric acid as external standards, respectively. The electrochemical data were obtained from the PAR system. Elemental analyses were performed at the Chung-Shan Institute, Lung-Tan, Taiwan.

Reaction of Uranium Tetrachloride with Tetrasulfur Tetranitride

Uranium tetrachloride (2.0 g) was added to a round-bottom flask containing 2.0 g of tetrasulfur tetranitride dissolved in 150 ml of benzene under nitrogen atmosphere and then refluxed for 3 days. The reaction mixture was separated by sinter fritted filter glass, the orange colored solution was discarded, whereas the dark-brown solid was washed with benzene and chloroform. The solid was extracted using a Soxhlet extractor with ethyl alcohol for 2 days under nitrogen atmosphere, and the solvent was evaporated *in vacuo*, with final washing in n-pentane to yield 46% of a dark-brown solid which was characterized as $Cl_2U(S_4N_4)$. *Anal.* Found: S, 27.1; N, 10.7; Cl, 13.5; U, 51.0. Calc.: S, 26.0; N, 11.3; Cl, 14.4; U, 48.3%. The infrared spectral data showed absorptions at 1400(s), 1200(w), 1096(w), 1034(w), 901(m), 493(w), and 468(w). The ^{14}N NMR spectra showed an absorption at 346.72 ppm, upper field with respect to the external standard of HNO_3. The cyclic voltammetric data showed the reductive potential at 0.9 V.

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Reaction of Tetrasulfur Tetranitride with Uranium Powder

(1) One hundred milliliters of a benzene solution of 1.5 g of tetrasulfur tetranitride were added to the designed apparatus containing 2.0 g of the highly reactive uranium powder, then refluxed for 48 h when the reaction mixture turned from orange to greenish yellow. After drying, mass data of the mixture proved it contained sulfur.

(2) One hundred milliliters of a benzene solution of 0.5 g of tetrasulfur tetranitride were added to the same apparatus containing 2.0 g of the highly reactive uranium powder, then reacted for 24 h. After drying, the infrared spectral data showed absorptions in addition to the absorptions of S_4N_4, at 1400(s), 426(w), and 402(w) cm^{-1}.

Reaction of Triscyclopentadienyl Uranium Chloride with Aluminum Chloride in Benzene Solution

A benzene solution of triscyclopentadienyl uranium chloride was added to a round-bottom flask containing a benzene solution of aluminum chloride in a molar ratio of 1:1. The reaction mixture was refluxed for 60 h until the red–brown solid precipitated out and this was filtered. The solid was removed and washed with benzene using a Soxhlet extractor (all operations were in a glove box) and then dried *in vacuo*. The compound was extremely hygroscopic and air sensitive. *Anal.* Found: C, 25.76; H, 2.97; Cl, 19.13. Calc. for $UCp_3Cl \cdot AlCl_3 \cdot 4H_2O$: C, 26.70; H, 3.41; Cl, 21.06%. The infrared data showed absorptions at 3100(w), 1445(s), 1300(w), 1019(m), 818(s), 684(m), 490(m), 272(w) and 249(w). No suitable solvents were found to determine the ^1H NMR spectrum.

Reaction of Triscyclopentadienyl Uranium Chloride with Aluminum Chloride in a Mixed Solution of Benzene with Tetrahydrofuran

A mixed solution of 15 ml of tetrahydrofuran in 200 ml of benzene was added to the round-bottom flask which contained 2.0 g of $UCp_3Cl \cdot ClAlCl_2$, a red–brown solid, in a glove box under nitrogen. The reaction mixture was stirred for 2 weeks, then the resulting green solution was removed under vacuum to dryness. Green crystals were obtained after washing with benzene which were extremely hygroscopic and air sensitive. *Anal.* Found: C, 28.40; H, 4.38; Cl, 20.34. Calc. for $UCp_3ClClAlCl_2 \cdot THF \cdot 4H_2O$: C, 30.56; H, 4.15; Cl, 19.03%. The infrared data showed absorptions at 3010(w), 2960(s), 2910(sh), 1445(s), 1350(w), 1300(w), 1247(w), 1180(w), 1042(w), 1025(w), 1019(m), 1002(s), 921(w), 840(vs), 798(s), 676(m), 272(w) and 249(w). The ^1H NMR spectral data showed absorptions at 1.16, 1.26, −3.25(br) and −8.16(br) ppm, relative to TMS as internal standard.

Results and Discussion

π-(S_4N_4)UCl_2

Streitwieser has prepared an uranium cyclooctatetraene sandwich complex via active uranium from the decomposition of uranium hydride [9]. We also reported the uranium cyclooctatetraene complexes from the reaction of the highly active uranium powder via electroamalgamation with cyclooctatetraene [7]. The chemistry of tetrasulfur tetranitride with losses or gain of two electrons to form $S_4N_4^{2+}$ and $S_4N_4^{2-}$ ions shows aromaticity like $C_8H_8^{2-}$. Direct reaction of the uranium powder with tetrasulfur tetranitride to obtain a similar sandwich, π-S_4N_4, is conceivable, however, because of no suitable solvent for the separation and purification of the reaction mixture, no attempt was made beyond spectral measurements on the mixture. The characteristic infrared absorptions of the mixture were at 1400, 426 and 402 cm^{-1}. In addition, the absorptions gradually disappeared on exposure to air for several hours, whereas the intensities of the absorption of S_4N_4 at 1082(w), 937(s), 741(m), 703(s) and 565(s) increased, which might indicate formation of S_4N_4 coordinated uranium complexes. The reaction of UCl_4 with S_4N_4 gave solid evidence of this kind of complex. Elemental analyses for the brown solid resulted in the formula $UCl_2S_4N_4$. From the cyclic voltammetry results, the reduction potential for U(IV) → U(III) is 0.90 V *versus* SCE, corresponding to a one-electron transfer, as predicted by the Rande and Sevcik equation and in good agreement with previous data [10]. The ^{14}N NMR spectral data showed a single resonance absorption peak at 346.72 ppm, upper field with respect to nitric acid. These data indicate the environment of nitrogen is more electron-clouded than that of tetrasulfur tetranitride, resulting in an upper field shift, because the chemical shift of ^{14}N for tetrasulfur tetranitride is at 105.52 ppm. The tetrasulfur tetranitride group attached to the uranium should be that of anion $S_4N_4^{2-}$, which is an unstable dianion [13, 14]. Further evidence from infrared data shows a strong characteristic absorption at 1400 cm^{-1} which is assigned to the stronger S–N stretching frequency for the complex $UCl_2(S_4N_4)$ than that of S_4N_4. The complex was found to be thermally unstable. Usually the reaction of tetrasulfur tetranitride with metal ions does not form π-complexes [11, 12].

Uranium-bridging Complexes

The insoluble red–brown solid was obtained from the reaction of triscyclopentadienyl uranium chloride with aluminum chloride. The solid was extremely hygroscopic and moderately air sensitive. In the infrared data the absorptions observed were at 3100(w), 1445(s), 1019(m) and 818(s), which showed the aromatic cyclopentadienyl functional group. The elemental analyses indicate the composition to be $Cp_3UClClAlCl_2 \cdot 4H_2O$, which is probably a polymeric structure as reported previously [4].

The reaction of the red–brown solid with tetrahydrofuran produced green crystals. The crystals were extremely hygroscopic and moderately air sensitive. Elemental analyses indicate the composition to be $UCp_3ClClAlCl_2 \cdot THF \cdot 4H_2O$. In the infrared data, the absorptions at 3010(w), 1445(s), 1019(m) and 798(s) showed the presence of an aromatic cyclopentadienyl group. The absorptions at 2960(s), 2910(sh), 1247(w), 1042(w), 1025(w), 1002(s), 921(w) and 840(vs) were from tetrahydrofuran. The ^{27}Al NMR data showed that no obvious difference was observed for the green solid and $AlCl_3$ around 220 ppm (*S*/*N* small). This is reasonable because the green solid has the same type of bridging. The ^1H NMR absorptions at 1.16 and 1.26 ppm might be ascribed to the tetrahydrofuran adduct, with absorptions at −3.25 and −8.16 ppm (ratio 1.7:1) from the two different environments of aromatic cyclopentadienyls. An increase in temperature showed that the two absorptions approached closer, but did not collapse until around 100 ℃. The green crystals should be $Cp_3UClClAlCl_2 \cdot THF$, having a square pyramidal configuration with tetrahydrofuran in the sixth position to form an octahedral structure.

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