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Preparation and synthetic utility of $MCl_4(Me_2NCH_2CH_2NMe_2)_2$, where M is uranium or thorium

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Abstract

UCl_4 or $ThCl_4$ dissolves in a solution of $Me_2NCH_2CH_2NMe_2$ (tmed) in toluene to give green $UCl_4(tmed)_2$ or colorless $ThCl_4(tmed)_2$. Anion metathesis with Me_3SiBr or Me_3SiI gives $UBr_4(tmed)_x$ or $UI_4(tmed)_x$, where x lies between 1 and 2. The tmed complexes are useful synthons for other ligand complexes, as well as for $(MeC_5H_4)_3ThCl$ or $(MeC_5H_4)_4Th$.

1. Introduction

The coordination chemistry of the tetravalent halides of uranium and thorium with monodentate ligands has been extensively studied [1]. However, bidentate ligands have not been explored as extensively; with nitrogen ligands, 1:2 bipyridine and phenanthroline complexes have been mentioned, but the geometry of the eight-coordinate complexes in the solid state and the solution state properties are unknown [2]. The geometry of eight-coordinate molecules has been reviewed and two idealized geometries are commonest: D_{2d}-dodecahedron and D_{4d}-square antiprism [3]. The X-ray crystal structure of eight-coordinate $UCl_4(Me_2NCH_2CH_2NMe_2)_2$ ($UCl_4(tmed)_2$) has been published and the geometry is near that of an idealized D_{2d} dodecahedron, though no preparative details were given [4]. In this paper, we give the preparative details for $UCl_4(tmed)_2$ and related compounds of thorium.

2. Experimental details

All the operations were performed under argon. Elemental analyses were carried out by the microanalytical laboratory of the Department of Chemistry, University of California, Berkeley. Proton, C and P nuclear magnetic resonance (NMR) spectra were recorded on a Jeol FX90 instrument and referenced to Me_4Si for ^1H ($\delta = 0$), ^{13}C ($\delta = 0$), or to 85% H_3PO_4 for ^{31}P ($\delta = 0$), and reported with positive values to high frequencies of the reference.

2.1. $UCl_4(Me_2NCH_2CH_2NMe_2)_2$

To a suspension of UCl_4 (1.0 g, 0.0026 mol) in toluene (20 ml) was added the diamine (1.0 g, 0.0086 mol). The suspension was stirred until a homogeneous solution was obtained after about 4 h. The green solution was filtered and the volume of the filtrate was reduced to saturation. Cooling (−20 °C) gave large, green prisms which were collected, washed with pentane (5 ml) and dried under reduced pressure to yield 1.3 g (85%) of an amorphous powder with a melting point of 180 °C (dec.).

The complex was soluble in halogenated and aromatic hydrocarbons, and slightly soluble in aliphatic hydrocarbons and diethyl ether. The diamine was displaced by tetrahydrofuran to give a complex that we have not characterized. We found the following characteristics: ^1H NMR (toluene-d_8, 30 °C): δ 5.29 ($\nu_{1/2} = 340$ Hz, 6H), −6.48 ($\nu_{1/2} = 340$ Hz, 6H), −35.2 ($\nu_{1/2} = 350$ Hz, 2H), −59.4 ($\nu_{1/2} = 350$ Hz, 2H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −50 °C): (δ 23.1 (NMe_2, $\nu_{1/2} = 20$ Hz), −1.60 (NMe_2, $\nu_{1/2} = 20$ Hz), −95.6 (CH_2, $\nu_{1/2} = 20$ Hz); analysis, calculated for $C_{12}H_{32}Cl_4N_4U$: C, 23.5; H, 5.27; N, 9.15; found: C, 23.1; H, 5.41; N, 9.08; IR: 1301(m), 1281(m), 1236(m), 1185(w), 1167(m), 1119(m), 1101(m), 1076(m), 1040(m), 1011(s), 1002(s), 989(m), 949(s), 917(m), 791(s), 782(m), 720(m, br), 596(m), 494(m, br), 458(m, br) and 374(m) cm^{-1}.

2.2. $ThCl_4(Me_2NCH_2CH_2NMe_2)_2$

The complex was prepared in a manner similar to that of its uranium analog, and crystallized from toluene

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(−20 °C) as colorless prisms in an 80% yield with melting point 210 °C (dec.). We found the following characteristics: analysis, calculated for $C_{12}H_{32}Cl_4N_4Th$: C, 23.8; H, 5.32; N, 9.24; Cl, 23.4; found: C, 23.9; H, 5.23; N, 9.19; Cl, 22.8; the IR spectrum was essentially identical to that of $UCl_4(tmed)_2$; ^1H NMR (toluene-d_8, 28 °C): δ 2.74 ($\nu_{1/2}=1$ Hz, 12H), 2.33 ($\nu_{1/2}=15.3$ Hz, 4H).

2.3. $UCl_4(Me_2PCH_2CH_2PMe_2)(Me_2NCH_2CH_2NMe_2)$

To a solution of $UCl_4(tmed)_2$ (1.2 g, 0.0020 mol) in dichloromethane (20 ml) at −40 °C was added 1,2-bis(dimethylphosphino)ethane (dmpe; 0.3 ml, 0.0020 mol), and the solution was stirred at −30 °C for 1 h. The light green solution was filtered rapidly and the filtrate was concentrated at −40 °C to about 5 ml. Pentane (about 5 ml) was added, followed by rapid filtration and cooling to −80 °C. The bright green prisms were collected (−40 °C), washed with cold (−40 °C) pentane (5 ml) and dried under reduced pressure, giving a melting point of 90 °C (dec.). The yield was essentially quantitative. The dry crystals were stable at 20 °C for at least two weeks, though solutions decomposed above −20 °C. For spectroscopic studies, the complex was dissolved in solvents cooled to −70 °C, and the solutions were never allowed to warm above −30 °C. We found the following characteristics: ^1H NMR (CD_2Cl_2, −30 °C): δ 11.9 (s, 6H), Me_2N; 2.90 (s, 6H), Me_2P; 1.90 (s, 6H), PMe_2; −20.6 (s, 6H), Me_2N; −23.6 (s, 2H), PCH_2; −36.5 (s, 2H), PCH_2; −37.1 (s, 2H), CH_2N; −56.2 (s, 2H), CH_2N; analysis, calculated for $C_{12}H_{32}Cl_4N_2P_2U$: C, 22.3; H, 4.99; N, 4.34; P, 9.59; Cl, 21.9; found: C, 22.2; H, 5.45; N, 4.29; P, 9.60; Cl, 21.5.

2.3.1. $UBr_4(tmed)_{1-2}$

An excess of Me_3SiBr (3 ml) was added to $UCl_4(tmed)_2$ (0.56 g, 0.91 mmol) in a flask equipped with a greaseless stopcock. The suspension was stirred at 70 °C for 36 h, with periodic venting of Me_3SiCl. All the volatile materials were then removed under reduced pressure, and the solid residue was washed with toluene (2×20 ml). The resulting green powder was sufficiently pure for the synthesis of bidentate phosphine complexes of UBr_4. The compound was soluble in methylene dichloride and tetrahydrofuran (thf), and insoluble in aromatic and aliphatic hydrocarbons and diethyl ether. We found the following characteristics: yield, 0.64 g; melting point 160 °C; IR (Nujol, CsI) – 1267(m), 1216(w), 1160(w), 1121(w), 1100(w), 1070(w), 1037(m), 998(m), 975(m), 942(w), 888(m), 850(br, s), 796(m), 775(w), 746(m), 655(m), 625(w), 512(w), 470(w), 420(w) and 336(br, m) cm^{-1}; analysis, calculated for $C_{12}H_{32}Br_4N_4U$ (based on $UBr_4(tmed)_2$): C, 18.3; H, 4.05; N, 7.09; found: C, 16.9; H, 3.73; N, 5.39.

2.3.2. $UI_4(tmed)_{1-2}$

The procedure for the synthesis of this compound was identical to that of $UBr_4(tmed)_2$. The resulting orange powder was pure enough for the synthesis of coordination complexes of UI_4. The compound was soluble in thf, and insoluble in methylene dichloride, aromatic and aliphatic hydrocarbons and diethyl ether. We found the following characteristics: yield, 0.89 g (from 0.63 g $UCl_4(tmed)_2$); melting point, 140 °C; IR (Nujol, CsI): 1270(s), 1230(w), 1210(w), 1173(w), 1155(w), 1100(m), 1030(m), 972(m), 956(m), 860(br, s), 798(s), 775(w), 724(m), 700(w), 645(m), 598(w), 435(w), 355(w) and 335(w) cm^{-1}; analysis, calculated for $C_{12}H_{32}I_4N_4U$ (based on $UI_4(tmed)_2$): C, 14.7; H, 3.27; N, 5.73; found: C, 12.03; H, 2.76; N, 2.56.

2.3.3. $(MeC_5H_4)_3ThCl$

(a) To a solution of $ThCl_4$ (3.90 g, 10.4 mmol) in 100 ml of thf was added by syringe 21.0 ml (31.3 mmol, 1.49 M in thf) of $Na(MeC_5H_4)$. The mixture was then heated at reflux for 30 h. Subsequently, the solvent was removed under reduced pressure and the residue was extracted with toluene (2×100 ml) at 80 °C. The volume of the combined extracts was reduced *in vacuo* to about 80 ml. Cooling to −80 °C yielded white microcrystals of $(MeC_5H_4)_3ThCl$ (1.72 g, 32.7%) with melting point 199–202 °C. We found the following characteristics: ^1H NMR (C_6D_6; 30 °C): δ 5.99 (AA'BB', 6H); 5.84 (AA'BB', 6H); 2.23 (s, 9H) ppm; IR (CsI): 1485(m), 1350(w), 1260(w), 1240(w), 1065(w), 1045(w), 1025(s), 930(m), 885(w), 835(s), 780(s), 645(w), 610(w), 330(m) and 245(s) cm^{-1}; electron ionization mass spectra (EIMS): $M^+=504$ a.m.u.; analysis, calculated for $C_{18}H_{21}ClTh$: C, 42.8; H, 4.20; found – C, 43.2; H, 4.35.

(b) To a solution of $ThCl_4(tmed)_2$ (2.96 g, 4.88 mmol) in 50 ml of thf was added by syringe 16.3 ml of $Na(MeC_5H_4)$ (14.7 mmol, 0.90 M in thf). After stirring for 9 h, the solvent was removed under reduced pressure. The resulting solid was extracted with 150 ml of toluene at 70 °C. The volume of the toluene extract was reduced *in vacuo* to about 80 ml, and cooling to −80 °C yielded white microcrystals of $(MeC_5H_4)_3ThCl$ (1.50 g, 60.9%). The materials obtained using methods (a) and (b) exhibited identical physical and spectroscopic properties.

2.3.4. $(MeC_5H_4)_4Th$

To a solution of $ThCl_4(tmed)_2$ (3.47 g, 5.72 mmol) in 100 ml of thf was added by syringe $Na(MeC_5H_4)$ (22.5 ml 1.02 M in thf, 23.0 mmol). After stirring the resulting mixture for 4 h, the solvent was removed under reduced pressure. The white solid was extracted with 120 ml of toluene. After filtration of the toluene extract, toluene was removed under reduced pressure, yielding a white powder of $(MeC_5H_4)_4Th$ (2.67 g, 85.2%). The compound did not appear to melt up to 260 °C. We found the following characteristics: ^1H NMR (C_6D_6; 30 °C): δ 6.31 (AA'BB', 2H); 5.91 (AA'BB', 2H); 2.17 (s, 3H) ppm; IR (KBr): 1494(m), 1244(m), 1042(s), 932(w), 894(w), 865(s), 852(s), 783(s), 760(s), 657(w) and 602(s) cm^{-1}; analysis, calculated for $C_{24}H_{28}Th$: C, 52.5; H, 5.15; found: C, 52.6; H, 5.22; EIMS: $M^+ = 548$ a.m.u.

3. Results and discussion

UCl_4 slowly dissolves in a solution of tmed (at least three molar equivalents) in toluene to give a deep green solution. Large green crystals of $UCl_4(tmed)_2$ are obtained by cooling the solution to a low temperature, with yields of up to 80%. The compound melts with decomposition at 180 °C. It is soluble in aromatic and halogenated hydrocarbons, but only slightly soluble in aliphatic hydrocarbons or diethyl ether. Although the diamine complex is soluble in tetrahydrofuran, the ether displaces one or more diamines, though we have not been able to isolate a pure substance from this solvent.

The thorium complex $ThCl_4(tmed)_2$ was also prepared by stirring a suspension of $ThCl_4$ with $Me_2NCH_2CH_2NMe_2$ in toluene, followed by crystallization from toluene at low temperature in yields up to 80%. The colorless complex melts with decomposition at 210 °C and its solubility properties are similar to those of its uranium analog.

The solid state structure of $UCl_4(tmed)_2$ shows it to be eight coordinated. The geometry is close to that of an idealized D_{2d} dodecahedron, as shown by the shape parameters [4]. It is reasonable to suggest that $UCl_4(tmed)_2$ and $ThCl_4(tmed)_2$ are isostructural in the solid state, since the compounds have nearly superimposable IR spectra.

In solution, the tmed complexes are fluxional. The ^1H NMR spectrum of $ThCl_4(tmed)_2$ at +56 °C in toluene-d_8 shows two singlets at δ 2.74 ($\nu_{1/2} = 1$ Hz) and 2.41 ($\nu_{1/2} = 5$ Hz) in area ratio 3:1, owing to the N–Me and N–CH_2 protons respectively. Lowering the temperature to −40 °C results in the splitting of the N–Me protons into two equal area singlets at δ 2.80 and 2.67 ($\nu_{1/2} = 5$ Hz for each resonance), and the N–CH_2 protons appear as a pair of doublets centered at δ 3.01 and 1.47, with $\nu_{1/2} = 13$ Hz for each resonance and a doublet separation of 12 Hz.

Homonuclear decoupling shows that the doublets are related, since irradiation of one doublet causes the other doublet to collapse into a singlet. Clearly, the methyl and methylene protons are not equivalent, and each $Me_2NCH_2CH_2NMe_2$ group may be described by the spin system $X_3X_3'AA'BB'Y_3Y_3'$. The decoupling experiments show that the spectrum results from a single species in solution. The ^1H NMR spectrum in chloroform-d_1 is qualitatively similar to that in toluene. At +56 °C, a single resonance is observed at 300 MHz at δ 2.87 ($\nu_{1/2} = 1$ Hz) and, at −61 °C, the N–Me resonance appears as a pair of singlets at δ 2.85 and 2.84, while the N–CH_2 resonance appears as a pair of doublets centered at δ 3.45 and 2.28, with $J = 12$ Hz and $\nu_{1/2}$ for all the resonances being about 6 Hz.

The ^{13}C NMR spectrum of $ThCl_4(tmed)_2$ in toluene-d_8 supports the ^1H NMR spectral data. At 27 °C, two resonances are observed; a triplet centered at δ 58.7 ($J_{CH} = 134$ Hz) and a quartet centered at δ 50.9 ($J_{CH} = 136$ Hz). Lowering the temperature to −50 °C causes the methyl resonance in the $^{13}C\{^1H\}$ NMR spectrum to split into two equal area resonances at δ 52.4 and 49.6, though the methylene resonance remains a singlet. Thus, the methyl carbon atoms are non-equivalent, though the methylene carbon atoms are equivalent.

The NMR spectra of paramagnetic $(f^2)UCl_4(tmed)_2$ are related to those of the diamagnetic thorium analog, with the exception that all the coupling information in the paramagnetic molecule is lost. The ^1H NMR spectrum in methylenechloride-d_2 at −80 °C shows two equal area singlets at δ 17.6 and −17.0 ($\nu_{1/2}$ in each case of 10 Hz), resulting from the methyl protons, and two singlets at δ −51.4 and −90.0 with $\nu_{1/2}$ of 20 Hz each, resulting from the methylene protons. At 25 °C, the resonances occur at δ 4.65 and −6.73 ($\nu_{1/2} = 340$ Hz), and δ −32.7 and −58.8 ($\nu_{1.2} = 365$ Hz) for the methyl and methylene protons respectively. The $^{13}C\{^1H\}$ NMR spectrum at −50 °C in methylenechloride-d_2 shows three resonances at δ 23.1 ($\nu_{1/2} = 20$ Hz), −1.60 ($\nu_{1/2} = 20$ Hz) and −95.6 ($\nu_{1/2} = 55$ Hz) resulting from the non-equivalent methyl carbons and the equivalent methylene carbons respectively. The ^1H NMR chemical shifts in PhMe-d_8 at 30 °C were reported in Section 2.

At the present time, we do not know the precise mechanism for the fluxional processes, or if the process is inter- or intramolecular.

A uranium bromide complex can be prepared by stirring a suspension of $UCl_4(tmed)_2$ with an excess of Me_3SiBr at 70 °C for 1–2 days [5]. The green solid that is obtained is not soluble in aliphatic or aromatic hydrocarbons, though it is soluble in dichloromethane or thf. Combustion microanalysis shows that the constitution is between 1 and 2 diamines per UBr_4. A uranium iodide complex can be made similarly from neat Me_3SiI and $UCl_4(tmed)_2$. The stoichiometry of the iodide also lies between 1 and 2 diamine ligands per UI_4. The orange material is insoluble in aliphatic, aromatic and chlorinated hydrocarbons, though it dissolves in thf. Addition of more tmed to the reaction solution does not alter the stoichiometry of the isolated materials in either case. In this context, we have not been able to prepare $UCl_4(Et_2NCH_2CH_2NEt_2)_2$ or $UCl_4(1,2\text{-}(Me_2N)_2C_6H_4)_2$; UCl_4 in the presence of these diamines does not dissolve in boiling toluene.

Even though the uranium bromides and iodides are non-stoichiometric solids, they are useful in ligand metathesis reactions. For example, $UBr_4(tmed)_x$ or $UI_4(tmed)_x$, with two molar equivalents of $Me_2PCH_2CH_2PMe_2$ in toluene, gives $UBr_4(dmpe)_2$ or $UI_4(dmpe)_2$ respectively. These diphosphine complexes crystallize as 2:1 complexes and they maintain their integrity in solution. In the case of the chloride, the addition of $Me_2PCH_2CH_2PMe_2$ yields $UCl_4(dmpe)_2$ [6]. The addition of one molar equivalent of $Me_2PCH_2CH_2PMe_2$ to $UCl_4(tmed)_2$ at −30 °C in dichloromethane yields crystalline UCl_4(tmed)(dmpe), provided that the temperature does not exceed −30 °C, since warming gives $UCl_4(dmpe)_2$.

The thorium complex $ThCl_4(tmed)_2$ is also a useful synthon, since it acts as a soluble source of $ThCl_4$. This is an important advance, since $ThCl_4$ is brick insoluble in such solvents as thf. The uranium complex $UCl_4(tmed)_2$ provides no such advantage, since base-free UCl_4 is soluble in thf. The utility of $ThCl_4(tmed)_2$ in synthesis is shown in the following example.

Refluxing a suspension of $ThCl_4$ with three molar equivalents of $NaMeC_5H_4$ in thf for 30 h gives $(MeC_5H_4)_3ThCl$ contaminated by $(MeC_5H_4)_4Th$. Separation of the latter from the former gives $(MeC_5H_4)_4Th$ in an isolated yield of about 30%. In contrast, stirring a thf solution of $ThCl_4(tmed)_2$ with three molar equivalents of $NaMeC_5H_4$ at room temperature for 9 h yields $(MeC_5H_4)_3ThCl$ in a 60% yield; no $(MeC_5H_4)_4Th$ is observed. Using four molar equivalents of $NaMeC_5H_4$ with $ThCl_4(tmed)_2$ in thf gives $(MeC_5H_4)_4Th$ in a yield of 85%.

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