

# PATENT SPECIFICATION

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## (54) VOLATILE URANYL HEXAFLUORODACETOACETONATE COMPLEXES

(71) We, EXXON RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to compositions of matter comprising uranyl hexafluoroacetoacetate complexes. The complexes of this invention are volatile and are of value in, for example, the isotope separation processes described and claimed in our co-pending Application No. 19896/76, (Serial No. 1,553,287).

U.S. Patent 3,951,768 to Karl Gurs, describes the use of a CO<sub>2</sub> laser for the separation of isotopes. One of the compounds mentioned with others as possibly usable for the separation of uranium compounds is UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O. Therefore, this patent appears to suggest the use of a uranyl compound with a CO<sub>2</sub> laser for isotope separation. Since this compound is listed with others, including UF<sub>6</sub>, which do not absorb the light from the CO<sub>2</sub>, it is not clear what was intended to be taught. Nevertheless, a uranyl compound is mentioned. The specific uranyl compound mentioned above which is contained in the Gurs patent, however, is non-volatile in the sense that it decomposes and therefore cannot be employed in the vapor phase for isotope separation. In fact, most uranyl compounds decompose without vaporization when heated. There is an article by Bloor *et al* (Canadian Journal of Chemistry, 42, 2201—2208) which teaches the existence of a compound described as uranyl phthalocyanine, which is sublimable under a vacuum "below 0.01 mm pressure at 400—450°C." These conditions, however, are again quite unacceptable for use in isotope separation processes. The infrared spectra of the solid uranyl phthalocyanine was observed in a *Nujol* (Registered Trade Mark) mull and an absorption peak "in the 900 to 950 cm<sup>-1</sup> region" was observed and tentatively attributed to the uranyl group. This in the range of the CO<sub>2</sub> laser.

Uranyl containing compounds have also been reported by Schlessinger *et al* in the Journal of the American Chemical Society 75, pages 2446—8 (1953). Schlessinger *et al*, however, do not teach the use of these materials in isotope separation processes. In fact, the vapor pressure of Schlessinger's compound was reported to be only 0.0027 torr at a temperature of 130°C. In addition, Belford *et al*, Journal of Inorganic and Nuclear Chemistry, Vol. 14, pages 169—178, 1960, teaches the preparation and properties of bis-hexafluoroacetylacetone-UO<sub>2</sub> tetrahydrate. This material, however, again does not appear to be vaporizable since it decomposes on heating to only 58°C. Thus, this material is not useful in the isotope separation process disclosed below.

To be useful in isotope separation processes the uranyl compound must therefore form a stable vapor and have a significant vapor pressure at a relatively low temperature. The stable vapor species is a necessary part of any process which seeks to utilize selective excitation to produce a disequilibrium in an isotope specific manner and which seeks to destabilize only the selectively excited species. The second requirement which seeks to minimize the temperature at which the required high vapor pressure is achieved is invoked to minimize the hot band population which may lead to reduced selectivity in all steps of the process, i.e., not only is the selectivity of the excitation process reduced, but also that of the subsequent differentiation step leading to the collection of the product species.

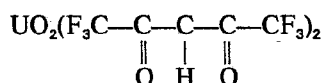
Use in a laser isotope separation process also imposes other properties upon the uranyl containing molecule. These include spectral transparency at the infrared and at the possible UV-visible excitation wavelengths. The vapor phase species should be a monomer to minimize the possibility of scrambling selectively absorbed energy. If possible, a molecule should be designed such that upon infrared or UV excitation an internal chemical rearrangement leading to stable final products separable from the starting material is obtained.

Finally, the energy expended in the vaporization process of the uranium bearing species should be minimized.

Another use which requires volatile uranyl compounds as described is in the separation of heavy metals by either gc (gas chromatography) or fractional sublimation. Such separations are important in mineral treatments and in reprocessing, in which uranium (present as uranyl ion) is to be separated from other rare earth metal ions, or other metal ions.

The present invention discloses a compound that has the above-mentioned properties, namely, uranyl hexafluoroacetylacetonate (hfacac) complexed with certain neutral monodentate ligands hereinafter defined.

Very little work has been reported on uranyl hexafluoroacetylacetonate (hfacac),



or its complexes. Hfacac, which is a chelating anion, is known to stabilize metal salts and allow for volatile species (Kutal, J. Chem. Ed. 52, 319 (1975)). Furthermore, this anion has no bands in the infrared region of 900—1000  $\text{cm}^{-1}$ , the region where the  $\text{UO}_2^{+2}$  group has a strong antisymmetric stretching mode, which is of interest for any isotope selective  $\text{CO}_2$ -laser irradiation.

In general, uranyl compounds preferred to have five atoms coordinated to the central U ion (in addition to the oxygens of the uranyl), see e.g., U. Casellato *et al*, *Inorganica Chimica Acta*, 18, 17 (1976). Since each hfacac group uses two coordination sites, this leaves one open site for a neutral ligand, which is necessary to produce a stable uranyl containing vapor. In the absence of an appropriate stabilizing neutral ligand it is impossible to generate the stable monomeric vapor of the uranyl (hfacac)<sub>2</sub> which would be necessary for an isotope separation process referred to above. The Belford *et al* paper, described above, shows that water molecules are not suitable as neutral ligand since the compound does not volatilize so as to form such a stable vapor phase species.

If no other molecules are present,  $\text{UO}_2(\text{hfacac})_2$  will dimerize, sharing two of the oxygens, and thus each  $\text{UO}_2^{+2}$  ion will have the requisite five oxygens around it. This dimer is not useful for laser isotope separations (monomers are preferred) because its volatility is too low and it allows for scrambling of absorbed energy and loss of selectivity. Energy absorbed by the selectively excited  $\text{UO}_2^{+2}$  group is diluted due to enhanced transfer to the second  $\text{UO}_2^{+2}$  group which is intimately bound to it in a dimer or oligomer. Therefore, judicious selection must be made to choose a neutral Lewis base molecule to stabilize the uranyl (hfacac)<sub>2</sub> as a monomer, to confer high volatility, and to have no infrared bands which might interfere with the  $\text{UO}_2^{+2}$  absorption. In addition, the presence of this neutral ligand may also enhance any subsequent photochemical reaction desirable in an isotopic selective process.

There have been reports of  $\text{UO}_2(\text{hfacac})_2\cdot\text{L}$  compounds in which L= aromatic amine oxides (Subramanian *et al*, J. Inorg. Nucl. Chem. 33, 3001 (1970)), phosphine oxides and sulfoxides (Sieck, Gas Chromatography of Mixed-Ligand Complexes of the Lanthanides and Related Elements, Ph. D. Thesis, Iowa State

Univ., (1971)). Because of relatively low vapor pressures, these substances are not suitable for use in isotope separation processes.

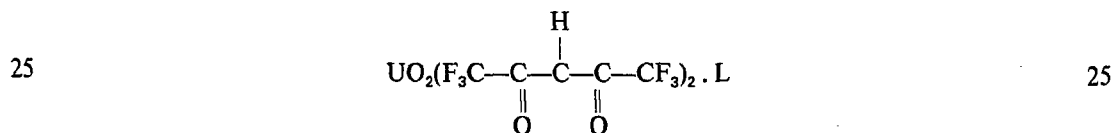
5 Mitchell (Synergic Solvent Extraction and Thermal Studies of Fluorinated Beta-Diketone-Organophosphorus Adduct Complexes of Lanthanide and Related Elements, Ph.D. Thesis Iowa State Univ., (1970)) prepared the tributylphosphate complex of  $\text{UO}_2(\text{hfacac})_2$  and showed that it sublimed at about  $150^\circ\text{C}$ . But, as discussed above, significant vapor pressures at lower temperatures are desired for any useful throughput in an isotope separation process. A sublimation temperature near or less than  $100^\circ\text{C}$ . is much preferred.

10 Very recently a comprehensive review of the complex chemistry of the actinides appeared in which the paucity of work on  $\text{UO}_2(\text{hfacac})_2$  and its complexes was evident (Casselato *et al*, Inorg. Chimica Acta, 18, 77 (1976)). One interesting fact in this review (p. 87) was that in all uranyl acetylacetonate-neutral ligand complexes studied, the ligand dissociates *prior* to sublimation. In contrast, the compositions of matter for use in the present invention must provide a stable in the vapor state after sublimation. The vapor phase molecule must be unchanged in the process of volatilization.

20 The search has, therefore, continued for such a composition of matter which would be useful in such isotope separation processes. Such compounds would thus provide a process where isotope separation could be carried out utilizing a  $\text{CO}_2$ -laser in a commercially acceptable manner.

The present invention provides a uranyl ion-containing composition of matter which can be utilized in processes for the separation of isotopes.

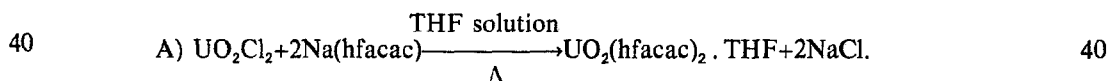
The compositions of matter of the invention have the formula



where L may be one of the following: ethanol, isobutanol, tert-butanol, methanol, tetrahydrofuran, acetone, ethyl acetate, n-propanol, isopropanol, and dimethylformamide.

30 These compositions may be prepared in the manner described below. In the following preparations, the compound  $\text{UO}_2(\text{hfacac})_2 \cdot \text{THF}$  will be the case described. Exactly the same procedure will hold to prepare the other compounds, substituting for THF the compounds methanol, ethanol, *i*-propanol, *i*-butanol, *t*-butanol, n-propanol, dimethylformamide, ethyl acetate, and acetone. Once any one of the compounds is prepared, any other may be prepared from it by the process of ligand exchange, that is, by treating the first composition with an excess (greater than about 50 molar) of the ligand to be substituted, and evaporating off the excess ligand and replaced ligand.

35 Three different methods to prepare  $\text{UO}_2(\text{hfacac})_2 \cdot \text{THF}$  have been found to work, and are discussed below.



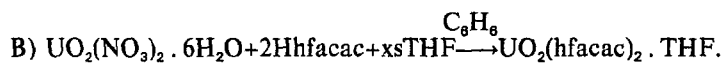
Anhydrous uranyl chloride is combined with about 2 mole equivalents of sodium hexafluoroacetylacetonate dissolved in tetrahydrofuran which functions as the solvent and as the neutral ligand.

45 A solvent, THF, in an amount of at least 1 mole is used for each mole of uranyl chloride. More than one mole may be used to increase dissolution.

The uranyl chloride concentration in the solvent may vary from 0.01 to 14 moles/liter. A preferred concentration range is between 0.1 and 3 moles/liter.

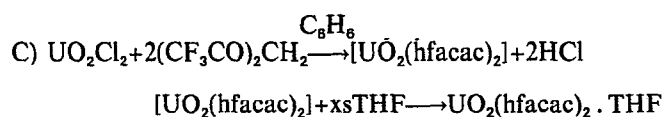
The reaction may be refluxed at the boiling point of THF for a period of time to increase the rate of the reaction (less than 24 hours).

50 The desired product formed is soluble in the solvent and the product and solvent are isolatable by filtration from the sodium chloride which is insoluble in the solution. The excess solvent is evaporated (under nitrogen) leaving the product.



A uranyl salt such as uranyl nitrate is dissolved in a sufficient amount of water at ambient temperatures. The pH should be maintained between 0 and 7 and may be adjusted by the addition of inorganic acids like HCl or HNO<sub>3</sub>. The concentration of the uranyl salt may range between 0.001 to 10.0 moles/liter.

5 In a separatory funnel, this solution is added to a solution of benzene containing at least two mole equivalents of hexafluoroacetylacetone and at least one mole equivalent of the neutral ligand, THF. A volume of benzene approximately equal to the volume of water is used. After shaking the liquids and separating off the lower aqueous phase, which removes most of the water and other coproducts, the resulting benzene solution which contains the desired product is dried over anhydrous sodium sulfate. The sodium sulfate is removed and the benzene solution is evaporated to remove any excess water leaving the product. That is, the solvent may be removed by conventional vacuum distillation at ambient conditions or by stripping with a flowing nitrogen stream. The final product should preferably be stored in an inert atmosphere and shielded from light.



20 Uncomplexed uranyl hexafluoroacetylacetonate is first prepared by reacting uranyl chloride with at least two moles of the diketone in refluxing benzene. These operations are preferably conducted in the absence of air.

The uranyl chloride concentration, which is a slurry, ranges from 0.001 to 10 moles/liter and it is reacted with at least two mole equivalents of the diketone. HCl generated in the reaction is removed. The product, [UO<sub>2</sub>(hfacac)<sub>2</sub>]<sub>2</sub> is recovered after evaporating the benzene solvent. It is easily converted into the THF complex by being dissolved in at least 1 mole equivalent of the solvent, and it may be recovered as in Example A.

#### EXAMPLE 1

Preparation of UO<sub>2</sub>(Hfacac) · THF by Method A.

30 Anhydrous uranyl chloride (3.4 g, 10 millimol) is dissolved in 25 ml of THF, and to this solution is added 25 ml of a solution of 4.6 g (20 millimol) sodium salt of hexafluoroacetylacetone. The reaction is refluxed an hour, the sodium chloride is filtered off and the filtrate evaporated to yield about 7.5 g yellow solid, mp 85—86°C.

#### EXAMPLE 2

35 Preparation of UO<sub>2</sub>(Hfacac) · L by Method B.

5.0 g of uranyl nitrate (10 millimol) is dissolved in 100 ml water maintained at pH 3. In a separatory funnel this solution is added to 100 ml of a benzene solution containing 4.2 g hexafluoroacetylacetone and 5 ml of THF. After shaking the liquids and separating off the lower aqueous phase, the benzene solution resulting is dried over anhyd. sodium sulfate and evaporated, leaving 3.0 g yellow solid, mp 90°C.

#### EXAMPLE 3

Preparation of UO<sub>2</sub>(Hfacac) · L by Method C.

45 Uranyl hexafluoroacetylacetonate is prepared by refluxing uranyl chloride (3.4 g, 10 millimoles) in benzene (50 ml) with hexafluoroacetylacetone (8.3 g, 40 millimoles). The product is soluble in benzene and easily recrystallized from it. When dissolved in THF and evaporated to dryness, a yellow solid, mp 85—87°C remains.

50 All of the crude products obtained above were essentially identical. For the purposes envisioned for the compositions, they could be purified by one of two general methods, either by vacuum sublimation at about 0.1 torr (temperatures of 50—70°C), or by recrystallization from benzene or hydrocarbons such as hexane. In both cases nice yellow crystals were obtained, melting point, 92—92.5°C.

55 Elemental analysis for UO<sub>2</sub>(hfacac)<sub>2</sub> · THF, (MW 756) gave the following results:

	Calculated	Found
C	22.2	22.5
H	1.3	1.5
F	30.1	28.6

60 Mol wt by mass spectrometry is 756 and by cryoscopy in benzene is 752.

On repeated sublimations, the composition of the compound remained constant. That is, the neutral ligand remains bonded to the  $\text{UO}_2^{+2}$  group during and after vaporization (unlike other  $\beta$ -diketonates of  $\text{UO}_2^{+2}$  as described in Castellato, referred to above.)

The compositions described above were characterized (in addition to elemental analyses) by mass spectrometry, infrared and ultraviolet spectroscopy, and nmr spectroscopy. The melting points and sublimation temperatures, as well as the asymmetric stretching band in the infrared are summarized in Table I.

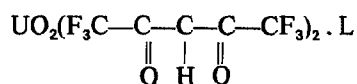
TABLE I  
Summary of the Complexes  $\text{UO}_2(\text{hfacac})_2 \cdot \text{L}$

L	mp ( $^{\circ}\text{C}$ )	Sublimation Temperature*	$\text{UO}_2^{+2}$ Infrared Absorption ( $\text{cm}^{-1}$ , benzene soln)
THF	92—92.8 $^{\circ}$	70 $^{\circ}\text{C}$	950
$\text{CH}_3\text{OH}$	117—120 $^{\circ}$	50 $^{\circ}\text{C}$	947
$\text{C}_2\text{H}_5\text{OH}$	110—115 $^{\circ}$	40 $^{\circ}\text{C}$	947
<i>i</i> - $\text{C}_3\text{H}_7\text{OH}$	128—129 $^{\circ}$	45 $^{\circ}\text{C}$	948
<i>i</i> - $\text{C}_4\text{H}_9\text{OH}$	51—55 $^{\circ}$	80 $^{\circ}\text{C}$	948
<i>t</i> - $\text{C}_4\text{H}_9\text{OH}$	105—177 $^{\circ}$	60 $^{\circ}\text{C}$	948
$\text{CH}_3\text{COCH}_3$	89—92 $^{\circ}$	55 $^{\circ}\text{C}$	948
ethyl acetate	58—63 $^{\circ}$	100 $^{\circ}\text{C}$	948

\* All had vapor pressures of at least 0.1 torr at 100 $^{\circ}\text{C}$ .

WHAT WE CLAIM IS:—

1. A composition of matter characterized by the formula



where L is a ligand selected from isopropanol, ethanol, isobutanol, tert-butanol, methanol, tetrahydrofuran, acetone, dimethylformamide, n-propanol and ethyl acetate.

2. A composition of matter as claimed in claim 1, wherein L is tetrahydrofuran.

3. A composition of matter as claimed in claim 1 or claim 2 and substantially as herein described.

4. A process for producing the composition of matter defined in claim 1, which comprises reacting uranyl chloride with a hexafluoroacetylacetonate dissolved in a said ligand L.

5. A process for producing the composition of matter defined in claim 1, which comprises forming an aqueous solution of a uranyl salt; adjusting the pH of said aqueous solution to between 0 and 7; combining the resultant aqueous solution with a solution containing hexafluoroacetylacetone and a said ligand L, and separating the said composition of matter which is thereby formed.

6. A process for producing the composition of matter defined in claim 1, which comprises reacting uranyl chloride with hexafluoroacetylacetone in the presence of a solvent to form uranyl hexafluoroacetylacetonate; separating the uranyl hexafluoroacetylacetonate from the solvent; and dissolving the uranyl hexafluoroacetylacetonate in a said ligand L to form the said composition of matter.

7. A process as claimed in any one of claims 4 to 6, wherein the ligand L employed is tetrahydrofuran.

8. A process as claimed in any one of claims 4 to 7 and substantially as herein described.

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