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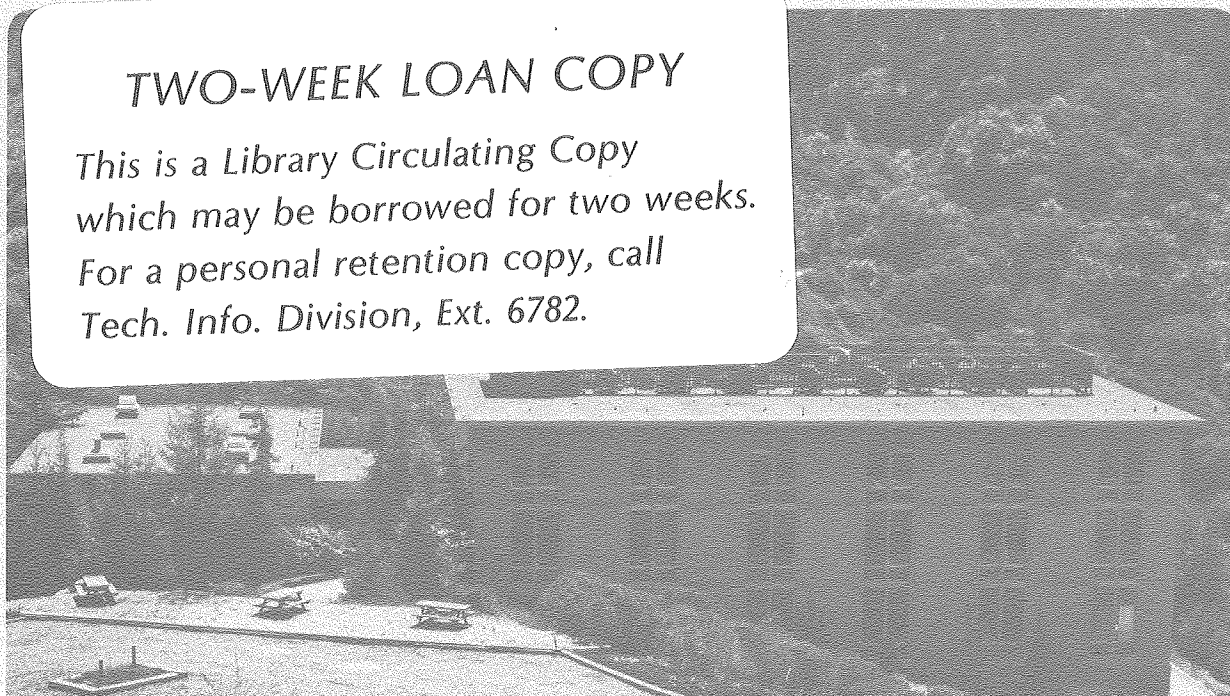
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SYNTHESIS AND PROPERTIES OF URANYL MONOTHIOCARBAMATE
ALKOXIDES, AN AIR-STABLE CLASS OF URANYL ALKOXIDES¹

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ABSTRACT

Uranyl monothiocarbamate alkoxides, $[\text{R}_2\text{NH}_2]^+ [\text{UO}_2(\text{R}_2\text{NCOS})_2\text{OR}']^-$, (where $\text{R} = \text{CH}_3$, C_2H_5 , and $n\text{-C}_3\text{H}_7$ and $\text{R}' = \text{CH}_3$ and C_2H_5) have been synthesized and characterized. The compounds, all yellow crystalline solids which are soluble in acetonitrile, alcohol, and other organic solvents, represent a class of both air- and moisture-stable actinide alkoxides and mixed monothiocarbamate-alkoxide metal ion complexes. Infrared spectroscopy indicates the title compounds to be associated in the solid state. X-ray photoelectron data using the uranium-4f, oxygen-1s, sulfur-2p, and nitrogen-1s photoelectron lines are in excellent agreement with known structural data and yield binding energies for the uranium-4f_{7/2}, 5/2 spin orbit doublet which are consistent with the hexavalent UO_2^{2+} species. The x-ray photoelectron data for the uranyl monothiocarbamate alkoxides are discussed with respect to possible canonical structures for the compounds, inductive charge effects involving the uranium-sulfur and uranium-oxygen bonds of the monothiocarbamate anion, and binding energies of sulfur and oxygen for other similar systems.

INTRODUCTION

In recent years much attention has been focused on the synthetic and structural chemistry of actinide complexes³ with much of it centered around the uranyl species. The uranyl ion, UO_2^{+2} , is rather unique⁴ in its chemistry, since the uranium-oxygen bond distances are markedly shorter than other uranium-ligand bond lengths involved in the equatorial coordination plane. Thus, in view of the large size of the uranium atom, the UO_2^{+2} ion for all practical purposes can be approximated to be a single particle rather than a triatomic cation. As a result of this size, the central uranium atom characteristically achieves high coordination numbers (typically, seven or higher) which lead to a wide array of unusual and varied complexes. Most of the work involving uranyl chemistry, however, has centered around the salts (and their complexes) such as the halides, nitrates, sulfates, and carboxylates⁵ and the most common organic chelating ligands such as tropolonates, acetylacetonates, and Schiff bases.⁶

Species such as carboxylates and other oxygen and nitrogen donor chelating ligands represent hard donor ligands bonded to the uranyl ion (as would be expected with the hard UO_2^{+2} cation⁷), and uranyl complexes in which sulfur, phosphorus, or other soft donor compounds are linked to UO_2^{+2} are rare.⁸ Solid complexes of the type $\text{UO}_2\text{L}_2\text{L}'$ (where L is the dithiocarbamate anion and L' is triphenylphosphine oxide or triphenylarsine oxide) have been prepared;⁹ other complexes

in the series $M^+UL_3^-$ ($M^+ = (CH_3)_4N^+$ and K^+ , and L^- is the dithiocarbamate anion) also have been made.¹⁰ The uranyl thioacetate complex with triphenylphosphine oxide has been studied by x-ray crystallography,¹¹ and the final structure reveals both sulfur atoms of the thioacetate group to be coordinated to uranium in a bidentate fashion.

Relatively few reports concerning uranyl alkoxides have been published other than the initial preparative work. The syntheses of the compounds for the most part follow the classical approaches for obtaining metal alkoxides, that is, the reaction of uranyl chloride with alkali metal alkoxides.^{12,13} Unfortunately, the uranyl alkoxides reported to date are hydrolytically unstable and thus must be manipulated in dry, inert atmospheres; furthermore, many of these alkoxides cannot be isolated as discrete, unsolvated compounds but rather as the alcoholate adducts such as $UO_2(OCH_3)_2 \cdot CH_3OH$ and $UO_2(OC_2H_5)_2 \cdot 2C_2H_5OH$.¹³ Bradley *et al.*¹³ have also reported solubility and solvolytic disproportionation problems, thus further hampering the preparation, isolation, and characterization of the compounds.

The compounds reported here represent a class of metal complexes in which both the monothiocarbamate and alkoxide anions are contained in the same molecule; the synthetic route utilized in their preparation represents an approach to making a uranyl alkoxide that does not require Schlenk equipment, vacuum lines, or other specialized anaerobic equipment. The monothiocarbamate alkoxides are air-stable, resistant to hydrolysis by atmospheric moisture, have a long shelf life (except for the $R=R'=CH_3$ derivative),

and may be dissolved in a number of solvents such as alcohols and acetonitrile in order to study their solution properties and reaction chemistry.

In addition to the straightforward reaction for the synthesis of an alkoxide and the unexpected stability toward air and moisture usually not associated with metal alkoxides, the compounds are also important from a structural, spectroscopic, and reaction chemistry standpoint. The uranyl monothiocarbamate alkoxides represent a case where the uranium-oxygen linkage is in three separate environments, i.e., the monothiocarbamate oxygen, the uranyl oxygen, and the alkoxide oxygen. The diethyl derivative ($R = R' = C_2H_5$)¹⁴ and the dipropyl derivative ($R = n-C_3H_7$, $R' = C_2H_5$)¹⁵ have been shown to consist of a five-coordinate equatorial plane perpendicular to the O-U-O axis in which the sulfur atoms of the monothiocarbamate ligands are adjacent to one another; the nitrogen atom of the ammonium cation in turn participates in cyclic hydrogen bonding with the oxygen atoms of the alkoxide and uranyl groups.

Since these complexes represent a structurally documented set of compounds, they have been used in this study as convenient models for infrared and x-ray photoelectron spectroscopy, two techniques which are applicable to solid state investigations of bonding in uranyl complexes. The n-propyl methoxide derivative ($R=n-C_3H_7$, $R'=CH_3$) has been shown¹⁶ to be a reactive material for the synthesis of uranyl monothiocarbamate disulfide, a mixed chelate-disulfide of uranium. Thus, the potential for an interesting and important reaction chemistry of the complexes is also quite large.

EXPERIMENTAL SECTION

Physical Measurements

Solid state infrared data were obtained in the 200–4000 cm^{-1} region on a Perkin-Elmer Model 283 infrared spectrometer using Nujol and Kel-F fluorocarbon mulls between KBr plates. Carbon, hydrogen, nitrogen, and sulfur analyses were performed by the analytical services laboratory of the chemistry department at the University of California, Berkeley. Decomposition mass spectra were obtained by a direct inlet ($\sim 100^\circ\text{C}$) on an AEI MS12 mass spectrometer utilizing an electron beam energy of 70 eV.

X-ray photoelectron spectra were recorded on a McPherson Model 36 spectrometer utilizing Mg K_{α} radiation (1253.6 eV). The peaks were fitted employing Lorentzian line shapes using a standard least-squares fitting program, and all binding energies were calibrated to the contaminant C_{1s} line using a value of $C_{1s} = 285.0 \text{ eV}$.¹⁷ Finely powdered samples were dusted on Scotch-brand tape and checked visually for decomposition after each set of spectra was obtained, but none was detected. The stability of the samples to radiation was further corroborated by the spectra being time-independent. The accuracy of all binding energies is $\pm 0.1 \text{ eV}$.

Materials and Synthesis of Compounds

Carbonyl sulfide (97.5 purity) and dimethylamine (99.0 purity) were obtained commercially from Matheson Gas Products, and reagent grade $\text{UO}_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ was purchased from Alfa Ventron Company and used as received. All solvents were reagent grade and used without further purification.

The uranyl monothiocarbamate alkoxides were prepared in essentially the same manner as that previously reported to synthesize the tris(monothiocarbamato)iron(III) derivatives¹⁸ (see Figure 1). Carbonyl sulfide was bubbled through a solution of five milliliters of the parent dialkylamine in ten milliliters of absolute methanol or ethanol, depending on which alkoxide was desired, in an ice bath with stirring. A saturated methanolic or ethanolic solution of $\text{UO}_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ was then added dropwise with stirring for several minutes with continued stirring until the yellow products precipitated. The compounds were filtered on a Buchner funnel, washed with several portions of cold diethyl ether, and air-dried on the filter bed. This procedure afforded products of high purity, as evidenced by elemental analyses. For subsequent measurements, however, the compounds were slowly recrystallized from acetonitrile at 0°C over a period of several days. All the complexes prepared, with the exception of the dimethyl methoxide derivative $\text{R} = \text{R}' = \text{CH}_3$, are stable to the atmosphere at room temperature for several months and slowly decompose over a very broad temperature range when heated in a capillary.

Analytical and Mass Spectral Data

$[(\text{CH}_3)_2\text{NH}_2]^+ [\text{UO}_2((\text{CH}_3)_2\text{NCOS})_2\text{OCH}_3]^-$: Anal. Calcd: C, 19.47; H, 4.14; N, 7.56; S, 11.55. Found: C, 19.03; H, 4.14; N, 7.33; S, 11.24.

Major mass peaks in mass spectrum (RA): COS^+ (78), $(\text{CH}_3)_2\text{NH}^+$ (75), $(\text{CH}_3)_2\text{NCO}^+$ (100).

$[(n-C_3H_7)_2NH_2]^+[UO_2((n-C_3H_7)_2NCOS)_2OC_2H_5]^-$: Anal. Calcd:
 C, 35.83; H, 6.65; N, 5.70; S, 8.70. Found: C, 35.72; H, 6.52; N,
 5.71; S, 8.34. Major mass peaks in mass spectrum (%RA): COS^+ (51),
 $(C_3H_7)_2NH^+$ (39).

$[(CH_3)_2NH_2]^+[UO_2((CH_3)_2NCOS)_2OC_2H_5]^-$: Anal. Calcd:
 C, 21.10; H, 4.39; N, 7.37; S, 11.26. Found: C, 21.14; H, 4.19; N,
 7.64; S, 11.02. Major mass peaks in mass spectrum (%RA): COS^+ (42),
 $(CH_3)_2NH^+$ (23), $(CH_3)_2NCO^+$ (100).

$[(n-C_3H_7)_2NH_2]^+[UO_2((n-C_3H_7)_2OCH_3)]^-$: Anal. Calcd:
 C, 34.85; H, 6.49; N, 5.80; S, 8.86. Found: C, 34.90; H, 6.48; N,
 5.92; S, 8.54. Major mass peaks in mass spectrum (%RA): COS^+ (40),
 $(n-C_3H_7)_2NH^+$ (30).

$[(C_2H_5)_2NH_2]^+[UO_2((C_2H_5)_2NCOS)_2OC_2H_5]^-$: Anal. Calcd:
 C, 29.46; H, 5.67; N, 6.44; S, 9.81. Found: C, 29.47; H, 5.64; N,
 6.42; S, 9.38. Major mass peaks in mass spectrum (%RA): COS^+ (52),
 $(C_2H_5)_2NH^+$ (66), $(C_2H_5)NCO^+$ (98).

RESULTS AND DISCUSSION

Infrared Spectra

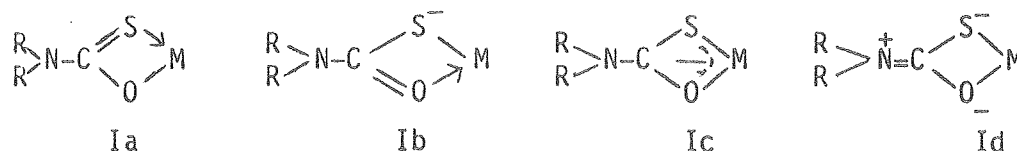
The infrared spectra of uranyl monothiocarbamate alkoxides are complex due to the rather large monothiocarbamate ligand which is present in conjunction with the alkoxide group; in addition, the hydrogen bonding of the alkoxide with the uranyl ion^{14,15} mentioned above and the overlap of several ligand vibrational modes in the same region also further complicate the interpretation in some instances. The metal monothiocarbamate complexes have not been so rigorously investigated spectroscopically as have the analogous dithiocarbamates. It is possible, however, to make moderately definitive, empirical band assignments on the basis of both previous work reported in the literature concerning similar ligand systems and structural data obtained in previous investigations. All infrared data, including band assignments, have been summarized in Table I.

The uranyl ion, UO_2^{2+} , assuming a linear symmetry of point group $D_{\infty h}$, has two normal modes of vibration that are routinely used in spectroscopic discussions^{19, 20}. In the present series of complexes, the asymmetric ν_3 band appears with moderate intensity in the 915-940 cm^{-1} region of the infrared spectrum, in excellent agreement with the position of this band in other uranyl complexes.²¹ In the case of the $R = n\text{-C}_3\text{H}_7$, $R' = \text{CH}_3$ derivative, $\nu_3(\text{UO}_2^{2+})$ appears at 915 cm^{-1} as a shoulder on the high-wavenumber side of the very strong 880 cm^{-1} methoxide absorption band along with a medium intensity band at 970 cm^{-1} . This band can be ruled out as a uranyl vibrational band,

since it also appears in the tris(monothiocarbamato)iron(III) propyl derivative^{18, 22} as well as di-n-propylamine.²² The infrared spectrum of the R = n-C₃H₇, R' = C₂H₅ derivative contains the shoulder band at 890 cm⁻¹ and the bands at 930 cm⁻¹ and 915 cm⁻¹, but the latter occurs as a separate, distinct absorption rather than as a shoulder. Both the second band at 915 cm⁻¹ present in the spectrum of this derivative and the band at 930 cm⁻¹ also may be assigned to the ν_3 mode, although the compound is virtually structurally identical to the R = R' = C₂H₅ compound which contains only one band at 937 cm⁻¹. Double resonances in the 900-1200 cm⁻¹ region have been observed for other uranyl complex systems²³ and are attributable to phenomena such as unit cell coupling.²⁴

The non-degenerate, symmetric ν_1 stretching frequency is infrared-forbidden but is known to occur¹⁹ as a weak band in the 790-900 cm⁻¹ region of the infrared in some uranyl compounds. A shoulder band at 890 cm⁻¹ can be found in the spectrum of the R = n-C₃H₇, R' = C₂H₅ compound, but one can probably safely rule this band out as the ν_1 mode on the basis of its strong intensity. Unfortunately, any complete and definitive assignment in this region is precluded due to the presence of the quite strong absorption of an alkoxide band in the 865-880 cm⁻¹ area. While this alkoxide band in the spectra of all the complexes exhibits asymmetry and quite obviously contains several small shoulder components, the total number of bands and their intensities is impossible to determine. Consequently, without detailed information concerning the value of ν_1 , discussions of relationships²⁵ concerning the uranium-oxygen bond force constants, bond distances, and bond orders in the UO₂⁺² species and the concomitant symmetric and asymmetric stretching frequencies are also ruled out.

The infrared spectra of dialkylmonothiocarbamate metal complexes are quite similar to their dithiocarbamate analogs. Dithiocarbamate derivatives have a characteristically strong infrared band in the 1450-1550 cm^{-1} region²⁶ which can be assigned as the $\nu(\text{C}\cdots\text{N})$ stretching frequency. This same vibrational mode is also found in the monothiocarbamates but is usually slightly broadened, since the $\nu(\text{C}-\text{O})$ stretching frequency is in the same region of the spectrum. Because the masses of the nitrogen and oxygen atoms are so similar, the two modes should also be highly coupled, making a separate assignment of the two bands quite difficult; the $\nu(\text{C}-\text{O})$ and $\nu(\text{C}\cdots\text{N})$ vibrational bands are thus usually assigned as one band in the 1400-1600 cm^{-1} region of the infrared spectra of the monothiocarbamates.²⁷ A frequency range such as that found for the $\nu(\text{C}\cdots\text{N})$ mode in both the mono- and dithiocarbamate complexes indicates an intermediate $\text{C}\cdots\text{N}$ bond order between one (1250-1350 cm^{-1}) and two (1640-1690 cm^{-1}).²⁸ If one explains the shortened $\text{C}\cdots\text{N}$ bond on the basis of electronic structures Ia-d as has been done for the corresponding dithiocarbamates,²⁹



it is evident that structure Id would result in a C-N bond order greater than one. Substituting the more electronegative oxygen for one of the sulfur atoms in dithiocarbamates should not diminish the

importance of these structures for the monothiocarbamates, and indeed x-ray crystallographic studies of the iron(III),³⁰ copper(I),³¹ and the present uranyl complexes^{14,15} have found C-N bond lengths of 1.33, 1.37, and 1.37Å, respectively, which are consistent with partial double bond character (C-N, ~1.46 and C=N, ~1.27Å).³² A canonical structure similar to Id, however, can be justified on structural grounds³³ and x-ray photoelectron data discussed below.

Although several workers³⁴⁻³⁶ have interpreted a $\nu(\text{C}\equiv\text{N}, \text{C}-\text{O})$ band in the 1503-1545 cm^{-1} range to indicate a bidentate monothiocarbamate ligand, x-ray crystallographic investigations³⁷ have shown this rule to be invalid in some cases. In the uranyl monothiocarbamate alkoxides, however, this combined band for the bidentate linkage in these compounds occurs between 1500 and 1530 cm^{-1} for all the compounds that have been studied here. This peak is slightly broadened with evidence of splitting into two or more bands in the spectra of all the complexes except the ($\text{R} = \text{n-C}_3\text{H}_7$, $\text{R}' = \text{C}_2\text{H}_5$) derivative in which it is observed to split into a single band at 1500 cm^{-1} with a second equally intense and slightly broader fused doublet or triplet in the 1502-1510 cm^{-1} region.

Other intraligand and coordination vibrational modes are also readily assigned, and in most cases they are quite similar to those reported earlier for other uranium complexes. The uranium-oxygen (monothiocarbamate oxygen) band has been reported at 455 cm^{-1} in the infrared spectrum of $\text{U}((\text{C}_2\text{H}_5)_2\text{NCOS})_4$,³⁸ comparing favorably with the 450-473 cm^{-1} range of values observed here for the same vibrational

mode. The uranium-oxygen (alkoxide oxygen) stretching frequency is found in the 390 cm^{-1} region, a value identical to that tabulated for terminal uranium-oxygen and bridging uranium-oxygen vibrations for uranium(VI) and uranium(V) alkoxides, respectively.³⁹ This assignment is further corroborated when one replaces OCH_3^- in $[(n\text{-C}_3\text{H}_7)_2\text{NH}_2]^+$ $[\text{UO}_2((n\text{-C}_3\text{H}_7)_2\text{NCOS})_2\text{OCH}_3]^-$ with the S_2^{2-} ligand;¹⁶ the band at 388 cm^{-1} in the original monothiocarbamate alkoxide disappears, while all other bands in that region are left unchanged.²² The characteristically sharp $\nu(\text{C-S})$ band appears in the spectra of all the complexes studied here in the narrow $665\text{--}670\text{ cm}^{-1}$ range; this is in excellent agreement with the value for this mode in other metal monothiocarbamate complexes⁴⁰ where this frequency has been shown to be somewhat independent of the central metal ion and occur in a rather narrow, fixed region of the spectrum.

X-RAY PHOTOELECTRON SPECTRA

There are very few published x-ray photoelectron spectroscopic (XPS) studies of uranium complexes relative to the number of papers in the literature dealing with compounds of the transition metals, but a few investigations have been carried out concerning the uranium oxides, several of the simple salts, and a limited number of complexes. The data obtained from the present study of the uranyl monothiocarbamate alkoxides represent the first reported in the literature for uranium(VI) existing in a UO_5S_2 metal coordination center and also the first data for a uranium chelate involving a uranium-sulfur bond. The present XPS study was initiated to determine if the uranium(VI) species in different coordination environments consisting of different donor atom sets yields spectra which exhibit different binding energies, photoelectron peak contours, and satellite structure associated with the uranium-4f photoelectron lines which have been utilized in previous XPS work with uranium. For purposes of detailed discussion concerning the physical appearance of the spectra of these compounds, the uranium-4f, oxygen-1s, sulfur-2p, and nitrogen-1s, spectral lines of the compound $[(C_2H_5)_2NH_2]^+[UO_2((C_2H_5)_2NCOS)_2OC_2H_5]^-$ are used, since detailed structural data¹⁴ are available; with the exception of minor variations in binding energies, the other complexes exhibit identical spectra. Binding energies have been tabulated in Table II.

Uranium-4f photoelectron lines

For any study of the x-ray photoelectron spectra of uranium complexes involving both sulfur and oxygen bonded to the central metal

atom, one first should find it helpful to compare the spectra of those complexes to those for compounds containing the individual ligand donor atom-uranium bond, or, in this case, the uranium oxides and the uranium sulfides. Although no XPS data concerning uranium-sulfur bonded complexes can be found in the literature, several studies involving uranium-oxygen systems do exist. Pireaux⁴³ and co-workers have investigated the oxides UO_2 , UO_3 , U_3O_8 and found that the different oxidation states of uranium in these compounds exhibit different "shake-up" satellite patterns located to the high binding energy side of the principal uranium-4f photoelectron lines. In the spectrum of uranium(VI) oxide, UO_3 , for example, in which uranium is hexapositive with only oxygen ligands (and thus a good potentially acceptable compound for uranium-oxygen bonding), these satellites, attributable to electronic excitation occurring from occupied ligand orbitals to an empty or partially filled metal electronic level,^{42,43} are observed at 3.7 and 10.6 eV to the high binding energy side of the uranium-4f_{7/2,5/2} peaks. The satellite located at 3.7 eV from the principal lines is a result of charge transfer from the ligand uranium-oxygen bonding band, which is predominantly of oxygen-2p character, to the empty uranium-5f orbital. This conclusion has also been corroborated by luminescence spectra.⁴⁴

The uranyl monothiocarbamate alkoxides exhibit photoelectron spectra which are strikingly similar to those seen for uranium(VI) having only oxygen as the ligand. The uranium-4f spectrum of $[(\text{C}_2\text{H}_5)_2\text{NH}_2]^+[\text{UO}_2((\text{C}_2\text{H}_5)_2\text{NCOS})_2\text{OC}_2\text{H}_5]^-$ shown in Fig. 2

consists of the uranium-4f spin-orbit doublet and the concomitant "shake-up" satellites associated with the principal photoelectron lines. Satellite sets d,b and c,a appear at ~ 3.5 – 3.7 and ~ 9.8 – 9.9 eV, respectively, to the high binding energy side of the main uranium lines and are thus in excellent agreement with shake-up patterns reported previously⁴¹ by Pireaux for uranium(VI)-oxygen systems. Consequently, it is both tempting and reasonable to assign these shake-up satellites to states localized to the UO_2^{+2} group. The full width at half maximum (FWHM) for the uranium-4f_{7/2,5/2} peaks in the spectra of all of the complexes studied here is 2.9–4.0 eV, which compares to a range of 2.1–3.2 eV for a series of compounds of varying uranium-oxygen composition,⁴⁵ with the largest width being found for γ - UO_3 .

Uranium-4f_{7/2} binding energies lie in the 381.0–381.4 range and are in quite good agreement with values reported for UO_3 (381.7 eV⁴⁶ and 381.9 eV⁴⁵) and $UO_2(CH_3COO)_2 \cdot 2H_2O$ (381.0 eV⁴⁶), the acetate salt representing another uranyl-oxygen bond in a chelated environment somewhat similar to that in the monothiocarbamate alkoxides. The great similarities in the photoelectron peak contours, satellite structure, and binding energies of the uranium-4f photoelectron doublet observed in the spectra of the present series of compounds, UO_3 , and $UO_2(CH_3COO)_2 \cdot 2H_2O$ seem to indicate very little correlation among the number, type, and coordination geometries of various ligands about the central metal ion and these spectral parameters. Uranyl acetate dihydrate, for example, consists of a coordination sphere in which uranium is surrounded by seven oxygen atoms donated by both

bridging and terminal acetate groups, one of the water molecules, and the uranyl oxygens,⁴⁷ while the compound γ -UO₃ used by Allen *et al.* has a complicated structure, consisting of two octahedral arrays with each array possessing its own primary and secondary bonds.^{48,49} All three compounds, however, yield spectra for the uranium-4f photoelectron lines which are strikingly similar.

Sulfur-2p, oxygen-1s, and nitrogen-1s photoelectron lines

Figure III shows the sulfur-2p_{3/2,1/2} spectrum for the R = R' = C₂H₅ derivative which consists of a two sub-level doublet (as a result of spin-orbit coupling) with an intensity ratio of 1:2 and an energy separation of approximately 1.2 eV, a separation in good agreement with previously reported spectra. The sulfur-2p binding energies for the complexes, tabulated in Table II, compare favorably with those in similar compounds. Several monothiocarbamate copper complexes, for example, exhibit sulfur-2p_{3/2} values such as 162.5 eV for the ((C₂H₅)₂NCS₂Cu^I)₄ tetramer,⁵¹ 162.4 eV for the ((C₂H₅)₂NCOSCu^I)₆ hexamer,⁵¹ and 162.2 eV for the monomeric ((C₂H₅)₂NCS₂)₂Cu^{II} chelate.⁵² One can see evidence of a small net charge transfer from the sulfur atoms to uranium as shown by the higher binding energies for sulfur in the uranyl monothiocarbamate alkoxides. The sulfur-2p binding energies reported in Table II are comparable to those reported for the Fe((C₂H₅)₂NCS₂)₃ complex⁵³ and a series of metal monothioacetates.⁵⁴ If one accepts a delocalized charge concept³³ for the uranyl-monothiocarbamate bonding, the change in the sulfur-2p binding energies would not be expected to be very great. The small chemical shifts

therefore reflect the chemical shift in binding energies which are shared among the sets of sulfur and oxygen ligand atoms bonded to the uranyl species. These small shifts in ligand atom binding energies are also consistent with previously reported x-ray photoelectron studies involving a common ligand complexed with a number of different cations.⁵⁵

The oxygen-1s photoelectron spectra of the complexes should reflect the variation in the bond strengths for the three separate bonding environments of oxygen to uranium, that is, the uranium-oxygen bonds involved in the uranyl, monothiocarbamate, and alkoxide species. It is quite reasonable to assume that the shortest bond distance, indicative of the strongest bond for one of the uranium-oxygen linkages (and thus the greatest charge dispersal away from the oxygen), should exhibit the highest binding energy, while the oxygen involved in the longest uranium-oxygen bond distance should give the lowest binding energy.

One structurally justified deconvolution of the oxygen-1s photoelectron spectrum for $[(C_2H_5)_2NH_2]^+[UO_2((C_2H_5)_2NCOS)_2OC_2H_5]^-$ is shown in Fig. 3. Based on the presumed validity of the correlation of the shortest U-O bond distance giving the highest binding energy, the three separate oxygen-1s lines at 532.0, 531.5, and 530.7 eV may be attributed to the uranyl, ethoxide, and monothiocarbamate oxygens, respectively. The U-O bonds in these three groups are 1.79, 2.20, and 2.38Å, respectively, in the $R = R' = C_2H_5$ derivative¹⁴ and exist in a 2:1:2 ratio, a ratio which is reflected in the deconvoluted spectrum.

The average binding energy for the three oxygen atoms in these environments is 531.4 eV (compared to 531.4 eV for the actual intermediate value of the ethoxide oxygen-1s line itself), while the average uranium-oxygen bond distance in the complex is 2.12Å.

The nitrogen-1s photoelectron lines have binding energies of 400.0 eV or less, values which are consistent with those previously reported for tertiary amines such as ethylenediaminetetraacetic acid (EDTA).⁵⁵ Studies of both charged (protonated) and neutral amine forms in this compound have revealed that the charged ammonium-nitrogen exhibits a nitrogen-1s binding energy which is ~2.5-3.0 eV higher than that observed for neutral, tertiary amines; this difference in binding energy and concomitant differences in charge of the two nitrogens has also been theoretically corroborated by other workers. On the basis of these data, along with the structural data previously mentioned,³³ canonical structure Id above can be discarded in favor of the delocalized model.³³ It is interesting to note, however, that even though there is an ammonium counterion present in the uranyl complexes reported here, the binding energies for the nitrogen-1s line are only ~400 eV; even deconvolution of the nitrogen-1s line into two separate lines to allow for the two different environments affords binding energy values considerably lower than those previously reported⁵⁵ for known, structurally documented cationic nitrogen forms. Presumably, this lowered binding energy reflects the participation of the ammonium ion in the hydrogen bonding scheme previously reported for these complexes.^{14,15}

Acknowledgments

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Table I. Infrared Data for $[R_2NH_2]^+[UO_2(R_2NCOS)_2OR]^-$ Complexes

Compound	Vibrational mode and position, cm^{-1}					
	$\nu(U-O)^a$	$\nu(U-O)^b$	$\nu(U-O)^c$	$\nu(O-R)$	$\frac{\nu(C \cdots N),}{\nu(C-O)}$	$\nu(C-S)$
$[(C_2H_5)_2NH_2]^+[UO_2((C_2H_5)_2NCOS)_2OC_2H_5]^-$	937(m)	455(s)	(d)	1045(s)	1500-10(s)	668(s)
				865(s)		
$[(n-C_3H_7)_2NH_2]^+[UO_2((n-C_3H_7)_2NCOS)_2OC_2H_5]^-$	915(m)	448(s)	(d)	1030(s)	1500-10(s)	668(s)
	930(m)			875(s)		
$[(CH_3)_2NH_2]^+[UO_2((CH_3)_2NCOS)_2OC_2H_5]^-$	930(m)	473(s)	390(s)	1050(s)	1520-30(s)	665(s)
				865(s)		
$[(CH_3)_2NH_2]^+[UO_2((CH_3)_2NCOS)_2OCH_3]^-$	930(m)	473(s)	390(s)	1055(s)	1520-30(s)	665(s)
				865(s)		
$[(n-C_3H_7)_2NH_2]^+[UO_2((n-C_3H_7)_2NCOS)_2OCH_3]^-$	915(m)	450(s)	388(s)	1055(s)	1510(s)	670(s)
				880(s)		
NaOCH ₃	-	-	-	1062(s)	-	-
NaOC ₂ H ₅	-	-	-	1062(s)	-	-
				882(s)		

a Asymmetric (ν_3) U-O mode of UO_2^{2+} ion

b Monothiocarbamate U-O mode

c Alkoxide U-O mode

d Obscured, below cutoff of KBr

Table II. X-Ray Photoelectron Data for $[R_2NH_2]^+[UO_2(R_2NCOS)_2OR^-]$ Complexes

Compound	Binding energies, eV ^{a,b}			
	U _{4f} _{7/2,5/2}	S _{2p} _{3/2,1/2}	O _{1s} ^c	N _{1s}
$[(C_2H_5)_2NH_2]^+[UO_2((C_2H_5)_2NCOS)_2OC_2H_5]^-$	381.1(3.5)	162.1(1.9)	532.0(2.2)	399.9(3.3)
	392.1(3.4)	163.2(1.8)	531.5(1.2)	
			530.7(1.8)	
$[(n-C_3H_7)_2NH_2]^+[UO_2((n-C_3H_7)_2NCOS)_2OC_2H_5]^-$	381.0(3.3)	162.2(2.4)	532.2(2.2)	399.9(3.3)
	391.9(3.5)	163.4(2.5)	531.5(1.6)	
			530.7(2.5)	
$[(CH_3)_2NH_2]^+[UO_2((CH_3)_2NCOS)_2OC_2H_5]^-$	381.2(2.9)	162.2(1.8)	532.2(2.2)	400.0(2.0)
	392.1(3.1)	163.5(1.8)	531.7(1.3)	
			531.0(1.8)	
$[(CH_3)_2NH_2]^+[UO_2((CH_3)_2NCOS)_2OCH_3]^-$	381.4(2.9)	162.2(1.8)	532.5(1.8)	400.0(2.3)
	392.3(3.1)	163.5(1.7)	531.7(1.1)	
			531.1(1.7)	
$[(n-C_3H_7)_2NH_2]^+[UO_2((n-C_3H_7)_2NCOS)_2OCH_3]^-$	381.3(3.6)	162.5(2.1)	532.2(1.7)	400.0(3.1)
	392.2(4.0)	163.8(1.9)	531.5(1.3)	
			530.8(2.5)	

^a Numbers in parentheses by binding energies represent the full width at half maximum (FWHM) for the principal photoelectron lines

^b Calibrated against the carbon 1s line taken as 285.0 eV.

^c The different values of the oxygen 1s photoelectron line represent the three different uranium-oxygen environments. Please see text.

FIGURE CAPTIONS

Figure 1. Synthetic scheme for uranyl monothiocarbamate alkoxides.

Figure 2. The uranium-4f and nitrogen-1s x-ray photoelectron spectra of $[(C_2H_5)_2NH_2]^+ [UO_2((C_2H_5)_2NCOS)_2OC_2H_5]^-$.

Figure 3. The oxygen-1s and sulfur-2p x-ray photoelectron spectra of $[(C_2H_5)_2NH_2]^+ [UO_2((C_2H_5)_2NCOS)_2OC_2H_5]^-$.

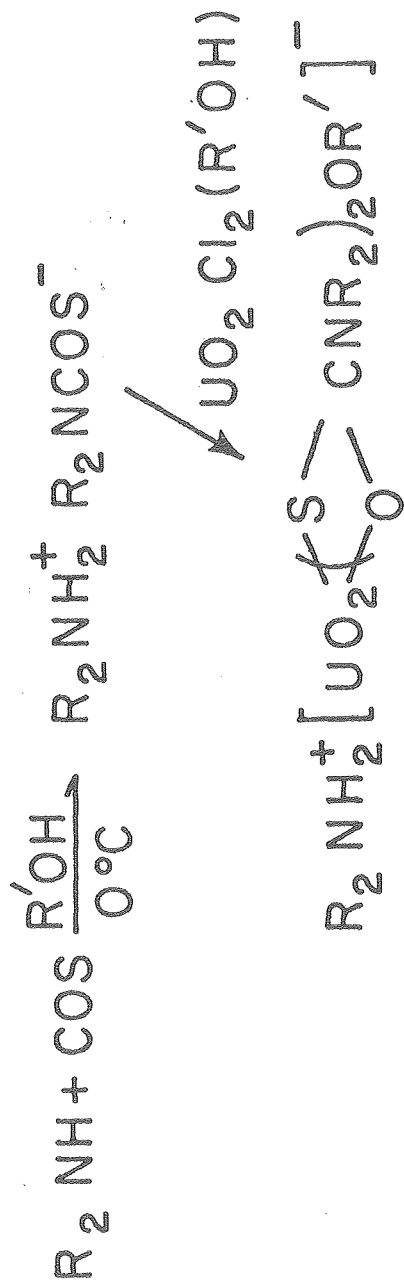
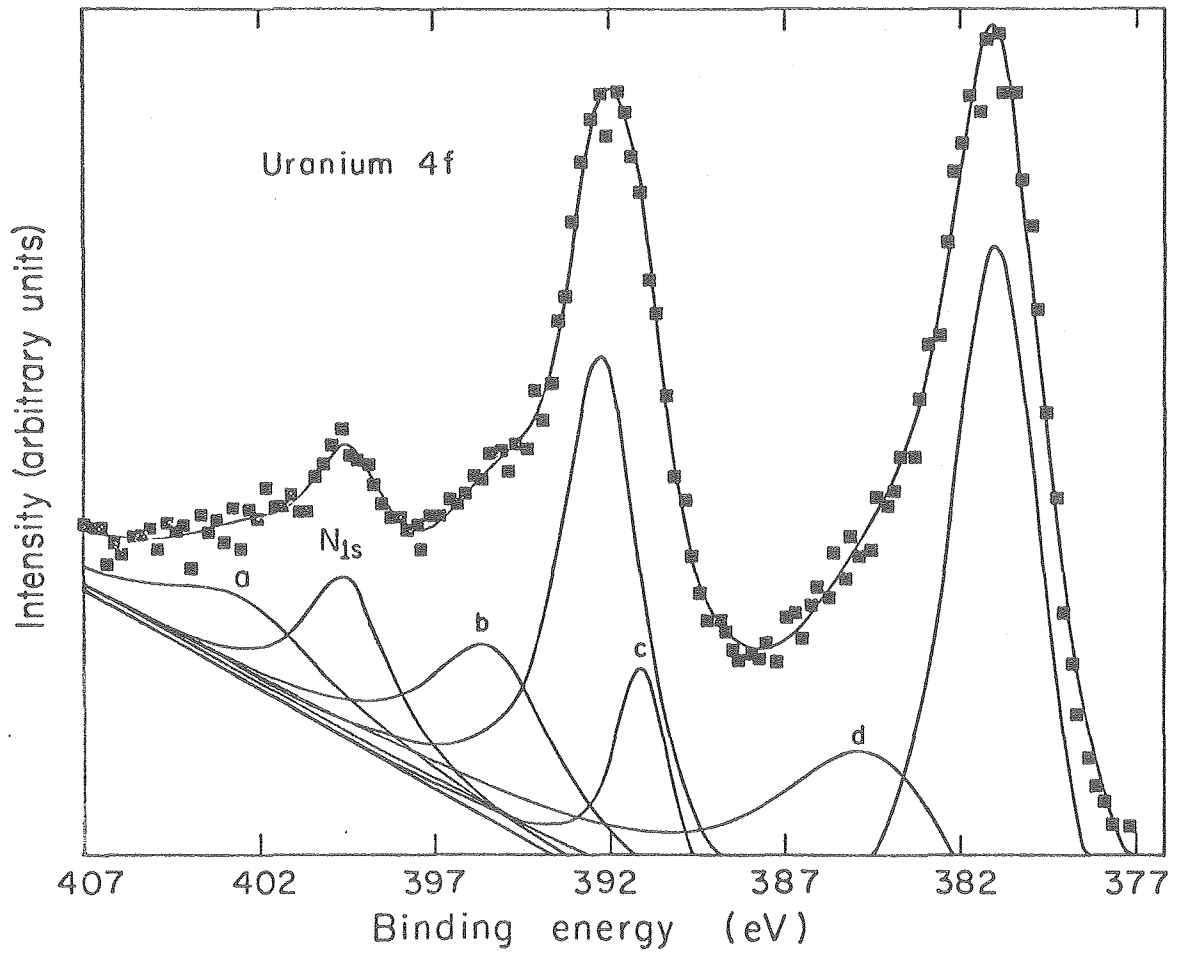


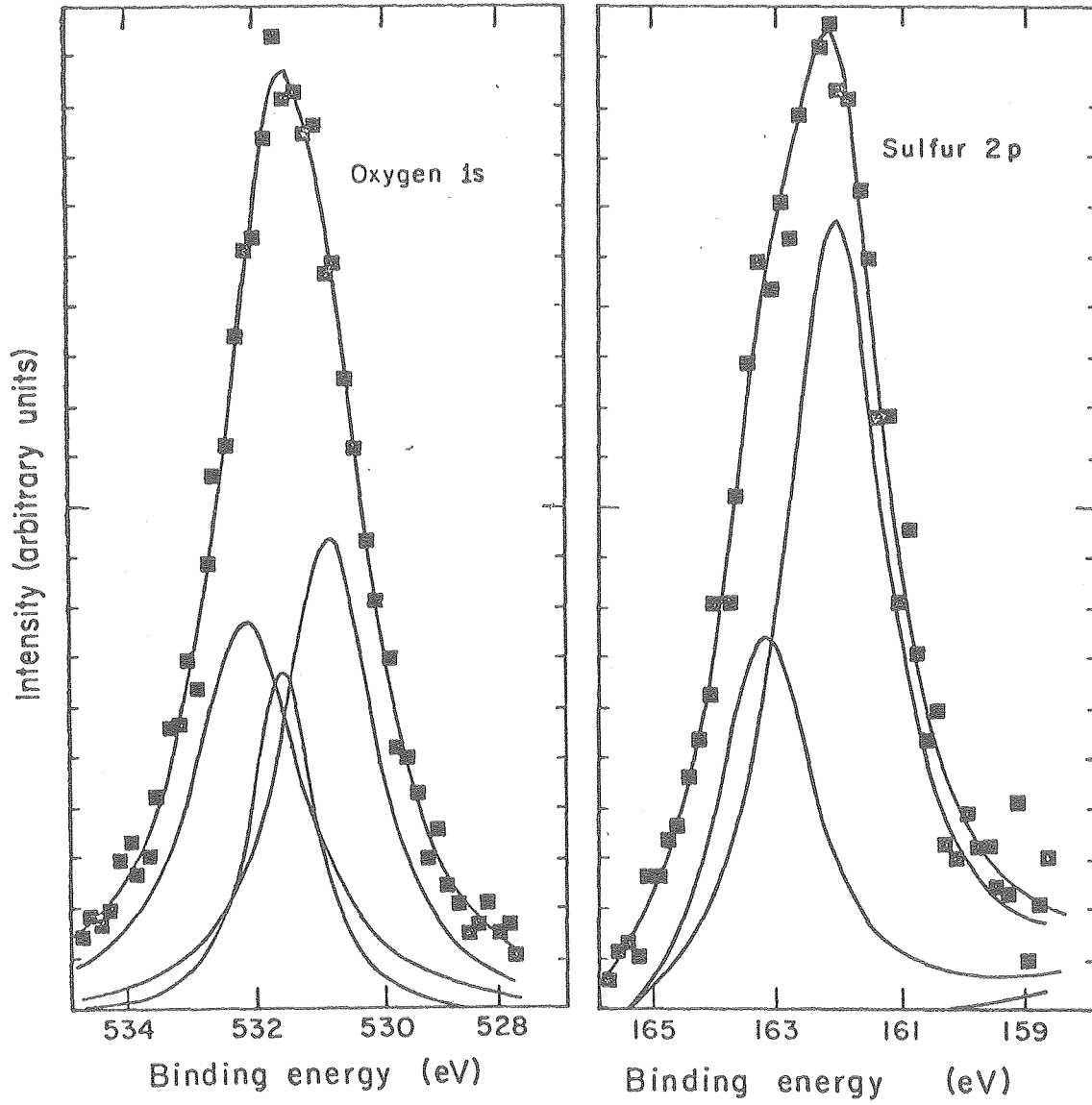
Figure 1.

Figure 2.



XBL785-800

Figure 3.



XBL785-799