which was trapped at −78 °C and a more volatile mixture of $(CF_3)_3PF_2$ and $(CF_3)_3P$ (0.177 g) identified by their NMR spectra.[19,31,35] An unidentified yellow-brown solid (0.034 g by difference) remained in the reaction vessel.

(b) A sample of $(CF_3)_3PF_2$ (contaminated with a trace of $(CF_3)_3P{=}O$) (0.185 g, ca. 0.67 mmol) and $(CH_3)_3SiSCH_3$ (0.169 g, 1.41 mmol) were combined in an NMR tube. NMR spectra obtained on the mixture after reaction for 15 min at room temperature showed the presence of $(CF_3)_3P(F)(SCH_3)$ and trace amounts of $(CF_3)_3PO$, $(CH_3)_3SiF$, and $(CH_3)_3SiSCH_3$ but showed no signals which could be assigned to the disubstituted phosphorane $(CF_3)_3P(SCH_3)_2$.

Acknowledgment. We thank the National Research Council of Canada for financial support of this work and Dr. J. A. Gibson for some experimental assistance and helpful discussion. We are also indebted to Dr. T. Nakashima, Mr. T. Brisbane, and Mrs. L. Wong for assistance with NMR spectroscopic studies and we thank Dr. J. S. Martin for the use of NUMARIT.[36]

Registry No. $(CF_3)_3P(OCH_3)_2$, 51874-39-6; $(CF_3)_3P(F)OCH_3$, 59888-71-0; $(CF_3)_3P(F)SCH_3$, 51874-42-1; $(CF_3)_3P[N(CH_3)_2]_2$, 51874-38-5; $(CF_3)_3P(F)[N(CH_3)_2]$, 51874-41-0; $(CF_3)_3P(Cl)[N(CH_3)_2]$, 51874-40-9; $(CF_3)_3P(F)OSi(CH_3)_3$, 59888-72-1; $(CF_3)_3PCl_2$, 420-72-4; $(CH_3)_3SiN(CH_3)_2$, 2083-91-2; dimethylamine, 34285-60-4; $(CF_3)_3PF_2$, 661-45-0; $(CH_3)_3SiOCH_3$, 1825-61-2; $[(CH_3)_3Si]_2O$, 107-46-0; $(CH_3)_3SiSCH_3$, 3908-55-2; ^{31}P, 7723-14-0.

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Thiourea Adducts of Dimethylhaloarsines. Cationic Trivalent Arsenic

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Received March 22, 1976
AIC60227C

The reaction of dimethylhaloarsines (Me_2AsX; X = Cl, Br) with thiourea (tu) in aprotic solvents yields 1:1 and 1:2 addition compounds which are best formulated as $Me_2As(tu)^+X^-$ and $Me_2As(tu)^+X^-\cdot tu$. The cationic nature of the trivalent arsenic is evidenced by the ir and Raman spectra which show the presence of an As–S linkage but the absence of an As–X linkage. These adducts evolve dimethylhaloarsine when exposed to the atmosphere or when subjected to reduced pressure. The quantitative evolution of arsine was followed by differential thermal and thermogravimetric techniques (DTA, TGA). A stepwise loss of arsine is observed only from $Me_2As(tu)^+Br^-$. The enthalpy changes for the decomposition of adduct to yield tu and arsine are 19.1 and 18.0 kcal mol^{-1} for the 1:2 chloro and bromo adducts and 14.7 and 15.5 kcal mol^{-1} for the 1:1 chloro and bromo adducts.

Introduction

The interaction of thiocarbonyl compounds with trivalent arsenic halides has been studied to a very limited extent. Loh and Dehn[1] prepared the adduct $(PhNH)_2CS\cdot AsBr_3$ which they obtained from a methyl ethyl ketone solution of arsenic tribromide and the substituted thiourea. Only elemental analyses were reported by these authors. From aqueous solution Walter[2] obtained a thiourea adduct with arsenic trichloride in which at least one As–Cl bond was replaced with an As–thiourea bond according to eq 1. Another report[3] described

$$2(NH_2)_2CS + AsCl_3 \xrightarrow{H_2O} [(NH)(NH_2)CS]_2AsCl\cdot H_2O + 2HCl \qquad (1)$$

the interaction between diphenylthiocarbazone and ethyldichloroarsine to form a 1:1 adduct. In this spectroscopic investigation the product was not isolated. Recently, Williams[4] investigated the formation of complexes having the general formula $AsRX_2L$ [R is phenyl or X; X is Cl, Br, I; L is tetramethylthiourea or *N*,*N*-dimethylimidazolethione] and found by means of a single-crystal x-ray study that L was linked to As by S. In contrast, Oertel, Malz, and Holtschmidt[5] prepared an arsenic compound (eq 2) presumably containing

$$As(NMe_2)_3 + 3PhNCS \rightarrow As[PhNC(S)(NMe_2)]_3 \qquad (2)$$

N-bonded *N*-phenyl-*N'*,*N'*-dimethylthiourea.

Although As(V) cations[6] are well-known, only a few instances have been reported where the As(III) cation has been shown to exist. Phenothiazine and 10-chlorophenoxarsine react to form an ionic compound containing an As–S linked cation and chloride anion.[7] Sisler and co-workers[8] prepared and characterized the ionic compound, $[(CH_3)_2AsNH_3]^+Cl^-$.

The present work describes the preparation and characterization of cationic adducts of dimethylhaloarsines with thiourea.

Experimental Section

Methods. Infrared spectra were recorded with a Beckman IR-12 infrared spectrophotometer in the range 4000–200 cm^{-1}. Samples were prepared in the form of pressed KI or KBr pellets. Raman spectra of samples sealed in glass capillaries were recorded with a Cary 82 Raman spectrometer using the 5145-Å line from a Coherent Radiation Model 53 argon ion laser.

Nuclear magnetic resonance spectra were obtained with a Varian Associates T-60 NMR spectrometer and referenced to TMS as the internal standard.

Differential thermograms (DTA) were obtained on a Robert L. Stone Model KA-2H controller equipped with a J-2 furnace platform, an F-1D furnace, and an SH-11 Br2-ALZ sample holder. The differential ring thermocouple was composed of Platinel II and the reference thermocouple of Pt—Pt-Rh (10%). The data were obtained at a heating rate of 2.8 °C min^{-1} from ambient temperature to 240 °C with the samples under a flowing nitrogen atmosphere of 0.10 SCFH (standard cubic feet per hour). Both sample and reference material (aluminum) were weighed into aluminum dishes. Indium with a purity of 99.999% (mp 157 °C; ΔH(fusion) = 0.781 kcal mol^{-1})[9] was the reference material used for enthalpy calibrations.

Thermogravimetric analyses (TGA) were obtained with a Robert L. Stone TGA-3C analyzer equipped with an F-1C furnace and coupled to the control equipment. The samples were weighed into glass dishes and heated in an atmosphere of N_2 (0.075 SCFH) at the rate of 2.8 °C min^{-1}.

Melting points were obtained using a Thiele tube equipped with a mechanical stirrer and nichrome wire heater. Each sample was sealed in a glass capillary.

Microanalyses were performed by Galbraith Analytical Labs., Inc., Knoxville, Tenn.

Mass spectra were recorded by Dr. Ronald Grigsby, Department of Biochemistry, Texas A&M University, with a CEC-21-110 spectrometer operated at an ionizing potential of 70 eV and an ion current of 100 μA. The accelerating potential was 8 kV and the source temperature was 200 °C.

Materials. With the exceptions described below, all chemicals were reagent grade and used without further purification.

Dimethylchloroarsine was prepared from dimethylarsinic acid according to the method of van der Kelen and Herman[10] and purified by distillation (bp 106.5–108 °C; lit.[11] 107 °C) under a nitrogen atmosphere. Dimethylbromoarsine was similarly prepared and purified (bp 127–129 °C; lit.[12] 129 °C). Both materials were stored under N_2 in Teflon-lined vials.

Tetrahydrofuran (THF; stored over sodium metal) and acetone (stored over molecular sieves) were distilled just prior to use.

Bis(thiourea)dimethylarsine Chloride. To a magnetically stirred suspension of thiourea (tu) (0.816 g, 10.8 mmol) in 20 ml of hot THF, 1.00 ml of dimethylchloroarsine (11.0 mmol) was added. The tu dissolved readily and after a few minutes a white solid formed. The solution was cooled to room temperature and filtered; the solid was recrystallized from THF, washed with 10 ml of THF, and dried in a stream of nitrogen. The yield was 1.17 g (4.00 mmol; 37.0% based on tu). Anal. Calcd for $(CH_3)_2AsCl\cdot2(NH_2)_2CS$: C, 16.4; H, 4.79; N, 19.2. Found: C, 16.7; H, 4.80; N, 19.4. Weight loss under reduced pressure was 47.7% (calcd for loss of $(CH_3)_2AsCl$ 48.0%); mp 117–119 °C.

Bis(thiourea)dimethylarsine Bromide. This compound was prepared in a manner similar to that just preceding. The compound was recrystallized from acetone; mp 118–121 °C. Anal. Calcd for $(CH_3)_2AsBr\cdot2(NH_2)_2CS$: C, 14.2; H, 4.15; N, 16.6. Found: C, 14.4; H, 4.29; N, 16.5.

(Thiourea)dimethylarsine Chloride. To a magnetically stirred solution of 0.830 g of tu (10.9 mmol) in 10 ml of acetone, 2.00 ml of dimethylchloroarsine (21.5 mmol) was added. A white solid formed; this was collected and recrystallized from acetone. The fibrous white solid was dried briefly in a stream of N_2. The yield was 80.5% (based on tu). Anal. Calcd for $(CH_3)_2AsCl\cdot(NH_2)_2CS$: C, 16.6; H, 4.61; N, 12.9. Found: C, 16.8; H, 4.56; N, 12.9. Weight loss under reduced pressure was 65.4% (calcd for loss of $(CH_3)_2AsCl$ 64.9%); mp 130–132 °C.

(Thiourea)dimethylarsine Bromide. In procedures similar to those described above, white $(CH_3)_2AsBr\cdot tu$ was obtained; mp 109–112 °C. Anal. Calcd for $(CH_3)_2AsBr\cdot(NH_2)_2CS$: C, 13.8; H, 3.83; N, 10.7. Found: C, 14.0; H, 4.00; N, 10.8.

Results and Discussion

The preparation of the adduct molecules was found to proceed in a straightforward manner. The 1:1 (haloarsine:thiourea) adducts were prepared in acetone while the 1:2 adducts were prepared in THF. It is interesting to note that the 1:2 adducts could be recrystallized from acetone (bp 56.2 °C; dielectric constant 20.70 at 25 °C; dipole moment 2.72),[13] but attempts to recrystallize the 1:1 adducts from THF (bp 67 °C; dielectric constant 7.58; dipole moment 1.7)[14] resulted in the formation of the 1:2 adduct and its separation from the residual haloarsine. These adducts tend to lose haloarsine when exposed to the atmosphere at ambient temperature and care must be exercised in their handling and storage. Dimethylchloroarsine can be removed quantitatively from the 1:1 and 1:2 adduct at reduced pressure in a few hours (eq 3 and 4; X = Cl). Samples of the 1:1 and 1:2 bromo adducts

$$(CH_3)_2AsX\cdot2tu(s) \rightarrow (CH_3)_2AsX(g) + 2tu(s) \qquad (3)$$

$$(CH_3)_2AsX\cdot tu(s) \rightarrow (CH_3)_2AsX(g) + tu(s) \qquad (4)$$

still contain dimethylbromoarsine after several days of similar treatment.

Mass spectral analysis of the haloarsines indicated that arsine was lost between 30 and 80 °C [$Me_aAsX_b^+$ (X = Cl, Br; b = 1, a = 0, 1, 2; b = 0, a = 0, 1, 2), CH_2As^+, and $C_2H_4As^+$] and only above 90 °C was tu evolved [tu^+, NH_2CS^+, $NHCNH_2^+$, and S^+].[15] In no instance was a molecular ion peak observed.

Reaction of the adducts with solvents prevented adequate characterization by NMR. Indeed, the 1:1 bromo adduct reacted too rapidly with DMSO-d_6 and acetone-d_6 for data to be obtained, while the 1:2 bromo adduct was moderately reactive. In comparison with the bromo adducts the chloro adducts were much less reactive. In DMSO-d_6, slight downfield shifts (0.05–0.10 ppm) in methyl proton resonances and moderate (0.50 ppm) downfield shifts in N–H resonances were observed; both effects indicated increased proton acidity.

The thermal behavior of the arsine adducts was further studied by DTA and TGA analytical methods. The change in enthalpy for each process was obtained from DTA data.[16] These data are summarized in Table I. The adducts containing chlorine are more volatile and more easily dissociated than the corresponding bromine adducts.

The most pronounced difference in thermal stability occurs between the 1:1 and 1:2 adducts of the same haloarsine. As can be seen in Figure 1, the 1:1 adduct begins to lose dimethylchloroarsine near room temperature, while the 1:2 adduct is considerably more stable. The same trend is observed

Table I. Differential Thermal and Thermogravimetric Data

Compd	EOT[a]	PT[b]	ΔH[c]	% wt loss	ET[d]
$Me_2AsCl \cdot 2tu$	65	90	19.1	98.1	81–125
$Me_2AsBr \cdot 2tu$	77	99	18.0	99.6	91–141
$Me_2AsCl \cdot tu$	54	75[e]	14.7	97.2	68–117
$Me_2AsBr \cdot tu$			(15.5)		
Peak 1	57	73	6.8	102.1	70–88
Peak 2	86	99	8.8[f]	102.1	96–143

[a] Extrapolated onset temperature (°C). [b] Peak temperature (°C). [c] kcal (mol of compound)$^{-1}$; ±3.4%. [d] Extrapolated temperature range (°C). [e] Second peak temperature is 89 °C. [f] 17.6 kcal (mol of $Me_2AsBr \cdot 2tu$)$^{-1}$.

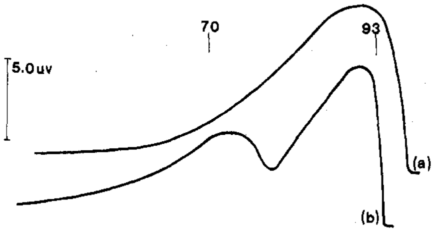


Figure 1. Differential thermal analysis data for (a) $[Me_2As(tu)]^+$-$Cl^- \cdot tu$ (1.02 mg) and (b) $[Me_2As(tu)]^+Cl^-$ (1.00 mg).

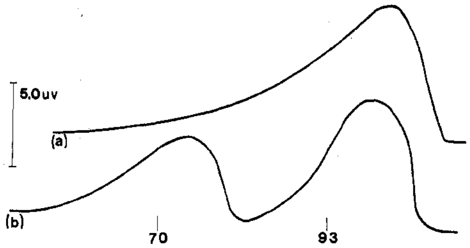


Figure 2. Differential thermal analysis data for (a) $[Me_2As(tu)]^+$-$Br^- \cdot tu$ (1.06 mg) and (b) $[Me_2As(tu)]^+Br^-$ (1.04 mg).

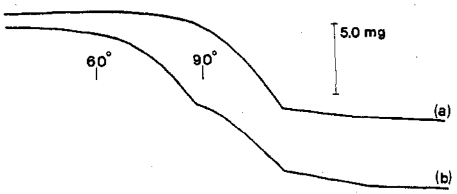


Figure 3. Thermogravimetric analysis data for (a) $[Me_2As(tu)]^+$-$Br^- \cdot tu$ (14.51 mg) and (b) $[Me_2As(tu)]^+Br^-$ (15.40 mg).

for the bromo adducts (Figure 2).

The DTA curve for the adduct (thiourea)dimethylarsine bromide (Figure 2) shows that two separate processes occur. The first process is attributed to the loss of $^1/_2$ mol of dimethylbromoarsine according to eq 5. Then, according to

$$(CH_3)_2AsBr \cdot tu(s) \rightarrow {}^1/_2(CH_3)_2AsBr(g) + {}^1/_2(CH_3)_2AsBr \cdot 2tu(s) \quad (5)$$

$${}^1/_2(CH_3)_2AsBr \cdot 2tu(s) \rightarrow {}^1/_2(CH_3)_2AsBr(g) + tu(s) \quad (6)$$

eq 6, the second process involves the loss of dimethylbromoarsine from the 1:2 complex formed in the first process. The change in enthalpy for this second process is 17.6 kcal (mol of $(CH_3)_2AsBr \cdot 2tu$)$^{-1}$, which compares favorably with 18.0 kcal (mol of $(CH_3)_2AsBr \cdot 2tu$)$^{-1}$ measured directly for $(CH_3)_2AsBr \cdot 2tu$.

The TGA data in Figure 3 corroborate the above findings. Dimethylbromoarsine is lost from (thiourea)dimethylarsine bromide in two separate steps. The first weight loss corresponds to the evaporation of $^1/_2$ mol of dimethylbromoarsine and the second corresponds to the loss of the remaining dimethylbromoarsine. The second weight loss occurs at the same temperature at which bromoarsine is lost from the 1:2 adduct.

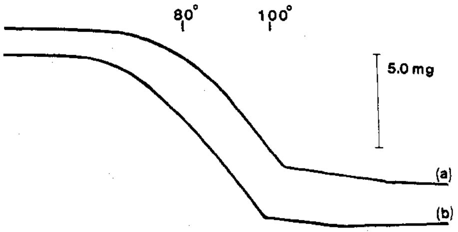


Figure 4. Thermogravimetric analysis data for (a) $[Me_2As(tu)]^+$-$Cl^- \cdot tu$ (18.31 mg) and (b) $[Me_2As(tu)]^+Cl^-$ (15.21 mg).

Table II. Raman Spectral Data (cm^{-1})

$(CH_3)_2$-$AsCl \cdot 2tu$	$(CH_3)_2$-$AsBr \cdot 2tu$	$(CH_3)_2$-$AsCl \cdot tu$	$(CH_3)_2$-$AsBr \cdot tu$
3295 m	3290 m	3130 m, br	3156 m, br
3170 m	3180 m	2990 s	2991 s
2995 m	2996 m	2903 vs	2911 vs
2915 s	2916 s	1415 w	1420 w
1633 vw	1637 w	1227 vw	1250 vw
	1612 w	1125 w	1116 w
1530 vw	1507 w	1086 vw	1081 vw
1460 vw	1475 w	702 m	704 m
1423 m	1433 m	579 s	581 s
1388 m	1393 m	567 s	573 s
	1388 w	470 m	471 m
1253 w	1253 w	402 w	405 w
1241 w	1245 w	305 vs	301 vs
1091 m	1093 m	245 vw	245 vw
738 ms	726 ms	212 w	214 w
705 w	707 w	187 w	187 w
590 m	584 m	130 w	145 w
582 ms	574 ms		
480 m	475 m		
456 s	445 s		
276 vs	274 vs		
113 m	163 m		

[a] Key: s, strong; m, medium; w, weak; v, very; br, broad.

The TGA data for the chloro adducts are shown in Figure 4. The 1:1 adduct loses chloroarsine at a lower temperature than the 1:2 adduct, but the arsine is lost in a single continuous step. Even when the heating rate was lowered to 1.5 °C min^{-1}, only a single weight loss was observed.

The DTA curve for the 1:1 adduct (Figure 1) shows that two processes occur but that they overlap and are difficult to resolve. Nevertheless, the second process possesses the same basic features shown in the DTA curve for the 1:2 adduct.

After haloarsine is vaporized from each sample, only tu remains. The residual tu exhibits a sharp endothermic peak corresponding to its fusion which overlaps with the broad endotherm corresponding to vaporization and decomposition. Each sample leaves a residue of ca. 7% of the tu present. tu, itself, behaves in a similar fashion.

Pertinent Raman data are presented in Table II. The data for the 1:2 chloro and bromo adducts are almost identical, as are those for the 1:1 compounds. The great similarities which exist between the Raman spectra of the chloro and bromo compounds are observed also in their ir spectra. However, because of their volatile nature, the preparation of suitable samples of the adducts for ir spectral measurement is difficult. Sample integrity can be maintained for Raman study when the samples are sealed in glass capillaries.

The general spectral features are those expected, but a brief discussion of the As–C stretching frequency is in order. This is because we have observed, in our continuing studies with organoarsenic compounds, that ν(As–C) for the methyl derivative is often located at a frequency which is considerably higher than that of the ethyl derivative but much closer to that of the higher homologues. For example, among the arsinic acids, $R_2As(O)OH$, ν_a(As–C) is located at 655 cm^{-1} for $(CH_3)_2As(O)OH$; the asymmetric stretching frequency falls

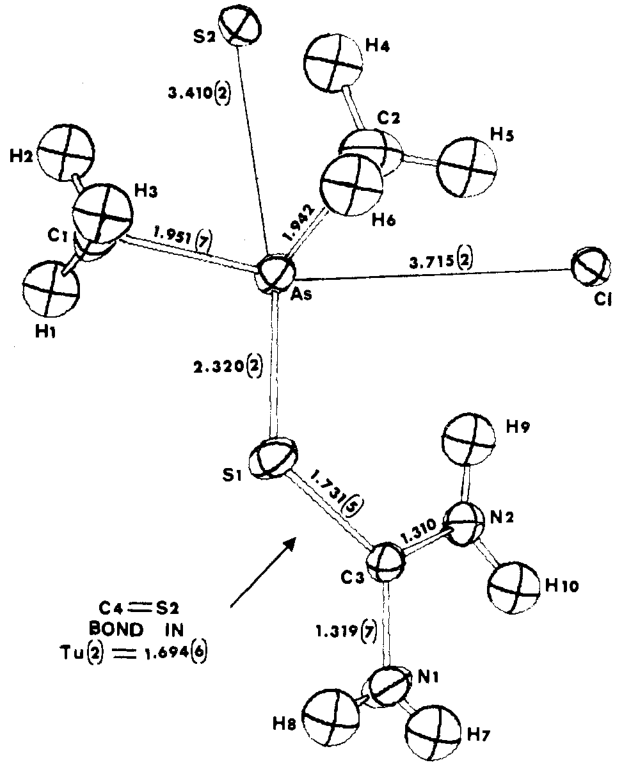


Figure 5. Structural features for the cationic portion of $[Me_2As(tu)]^+Cl^- \cdot tu$.

to 600 cm^{-1} for the ethyl derivative and then increases to 675 and 678 cm^{-1} for the *n*-propyl and *n*-butyl derivatives and remains close to this value through the C_{20} derivative. In the adducts which are the subject of this report, ν_a(As–C) is located over the narrow range 579–590 cm^{-1} while ν_s(As–C) is observed in the region from 567 to 582 cm^{-1} (Table II). There appears to be no absorption which can be assigned to an arsenic–halogen stretching mode. An As–Cl stretch would be expected at 361 cm^{-1} and an As–Br stretch would be expected at 265 cm^{-1}.[17] These bands are not present, although there is a very strong absorption at ca. 275 cm^{-1} for both 1:2 adducts and at ca. 303 cm^{-1} for both 1:1 adducts.

In order to better understand the discrepancy in Raman band assignments, a single-crystal x-ray diffraction study of bis(thiourea)dimethylarsine chloride was performed.[18] This study revealed there was no As–Cl bond. The chlorine is present as the chloride ion while the arsenic is bonded to sulfur. The salient structural features are reproduced in Figure 5. Thus, the Raman absorption which appears at ca. 275 cm^{-1} for the 1:2 adducts and at ca. 303 cm^{-1} for the 1:1 adducts can be assigned, with confidence, to the As–S stretch.

We were unable to prepare single crystals of the 1:1 adducts suitable for an x-ray crystallographic study. Hence, information concerning the As–S bond must be inferred from the ir and Raman data and the known similarities among the adducts. The As–S stretching mode for the 1:1 adducts is found about 30 cm^{-1} higher than that observed for the 1:2 adducts and may be a result of changes either in the bonding within the molecule or in its environment.

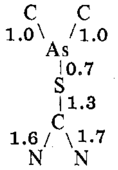
Arsenic in the cationic portion of bis(thiourea)dimethylarsine chloride is surrounded by three nearest neighbors, and by two atoms, Cl and S2, at longer distances (Figure 5). The chloride ion is at the expected van der Waals contact distance, while the distance to S2 (S from the second thiourea moiety) is only slightly shorter (0.4 Å) than the van der Waals contact distance.

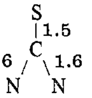
The close distances, As–C1 and As–C2, appear normal.[19] The short As–S bond is slightly longer than a "normal" As–S single bond,[19] and the C–S bond is somewhat lengthened compared with that in thiourea.

The relationship formulated by Pauling[20] between experimental bond length and single bond length and bond order is given in eq 7, where N is 0.71 for bond orders n between

$$D_n = D_1 - N \log n \qquad (7)$$

1 and 3 and is 0.60 for bond orders less than 1. With this formula and the known value of the As–S bond length, a bond order of 0.7 is calculated for the As–S bond in bis(thiourea)dimethylarsine chloride. Other bond orders within the cation and the second thiourea moiety are shown below.





As would be expected, the formation of an As–S bond weakens the C–S bond, and this change is reflected in the calculated bond orders. For comparison, Williams[4] found that the As–S bond distance in (*N,N*-dimethylimidazolethione)trichloroarsenic [$AsCl_3$(dmit)] is 2.304 Å. Thus, the As–S bond lengths are similar despite the following striking structural differences between the adduct $[Me_2As(tu)]^+Cl^- \cdot tu$ and the adduct $AsCl_3$(dmit): the thiourea adduct is cationic while that of Williams is neutral; in the thiourea adduct, arsenic is three-coordinate, while the other has four-coordinate As; the coordinated groups in the tu adduct are of low electronegativity while in the other case, groups of high electronegativity are attached to As. Moreover, the contrast in the ir and Raman data for the two types of adducts is striking. Williams[4] assigned a weak band at ca. 250 cm^{-1} to the As–S stretch in $AsCl_3$(dmit) while we assigned the very strong band at 276 cm^{-1} for the As–S stretch in $[Me_2As(tu)]^+Cl^- \cdot tu$. The strong absorption in our case helps in the location and identification of this band.

It seems clear that the correlation of the positions of spectral bands with the bond distances in molecules that contain As–S bonds is a very complicated matter. There exist gross structural differences between the adduct examined here and the adduct examined by Williams.[4] It would be highly speculative to infer that the As–S distance found in $[Me_2As(tu)]^+X^-$ is significantly shorter than the As–S distance in $[Me_2As(tu)]^+X^- \cdot tu$ on the basis of the relatively small differences in As–S frequency observed for the two compounds.

Acknowledgment. The authors express their appreciation to the Robert A. Welch Foundation, Houston, Tex., for financial assistance in support of this work.

Registry No. $(CH_3)_2AsCl \cdot 2tu$, 54912-40-2; $(CH_3)_2AsBr \cdot 2tu$, 59888-79-8; $(CH_3)_2AsCl \cdot tu$, 54912-39-9; $(CH_3)_2AsBr \cdot tu$, 59888-78-7; dimethylchloroarsine, 557-89-1.

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Synthesis and Characterization of a New Uranium(V) Compound: $H_3O^+UF_6^-$

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Received October 28, 1975 AIC50778N

The reaction of equimolar amounts of UF_5 and H_2O in hydrogen fluoride results in the partial dissolution of UF_5, yielding a blue-green solution from which the new salt oxonium hexafluorouranate(V) ($H_3O^+UF_6^-$) could be isolated as a green crystalline solid. Calorimetric measurements showed $H_3O^+UF_6^-$ to decompose at about 68 °C and its heat of formation to be equal to -628 ± 2 kcal mol^{-1}. Its ionic nature in the solid state and in HF solutions was demonstrated from vibrational and electronic spectra. The electronic spectrum is closely similar to those of $LiUF_6$, $NaUF_6$, and $CsUF_6$ and differs from those of $RbUF_6$ and KUF_6. This adduct shows a strong ESR signal, with $g = -0.78 \pm 0.10$, characteristic of UF_6^- salts. Based on its x-ray powder diffraction pattern, $H_3O^+UF_6^-$ is cubic with $a = 5.2229 \pm 0.0005$ Å.

Introduction

A recent work of Christe et al.[1] on H_3O^+ salts showed that the oxonium ion associates for instance with arsenic or antimony hexafluoro anions, forming the compounds $H_3O^+AsF_6^-$ or $H_3O^+SbF_6^-$. In previous researches, Bonnet et al.[2] made a DTA study of the solutions of antimony pentafluoride in HF–water mixtures and suggested the existence of ionized compounds $H_3O^+SbF_5OH^-$ and $H_5O_2^+SbF_6^-$. These facts, together with the well-known acidic properties of uranium pentafluoride[3] prompted us to look for the corresponding U(V) salt. This idea was further supported by some previous experimental observations that were made on the x-ray powder patterns obtained during the preparation of the compounds $M^{II}U^{V}{}_2F_{12}{\cdot}4H_2O$ (M^{II} = Co, Ni, Cu).[4] For some UF_5–HF–H_2O mixtures, a small amount of a new solid species was isolated and an x-ray diagram very close to that of $NOUF_6$[5] was obtained, but there was no reason for NO^+ to be present. Unfortunately, the amount of this compound was not sufficient to perform chemical analyses. Since the work of Christe,[1] it has become clear than an oxonium salt might have been obtained. The aim of the present paper is to describe the preparation of this salt (oxonium hexafluorouranate(V)) and some of its properties.

Experimental Section

Materials. Hydrogen fluoride (ultrapure grade) was supplied by Comurhex (Pierrelatte, France) in Monel vessels, under a 200 Torr fluorine pressure and was used without further purification. Uranium pentafluoride (β-UF_5) was prepared by mixing uranium tetrafluoride (Merck, nuclear grade) and uranium hexafluoride (from Comurhex) in liquid HF, at room temperature.[6] The purity of the UF_5 was checked by viewing its x-ray diffraction pattern.

Apparatus. The reactions were carried out in Voltalef (polychlorotrifluoroethylene) vessels, connected to a well-passivated Monel vacuum line. Solid materials were handled in a glovebox, under a dry nitrogen atmosphere.

The infrared spectra were recorded in the range 4000–250 cm^{-1} on a Perkin-Elmer Model 457 spectrophotometer or on a Beckman IR 9 apparatus (4000–400 cm^{-1}). In the far-infrared region, a RIIC (Research and Industrial Instruments Co., London) FS 720 (Fourier transform) spectrophotometer was used. In this case, samples were studied as mulls pressed between polyethylene disks. Otherwise they were pressed into pellets between silver chloride windows.

In the visible and near-infrared regions, spectra were obtained from hydrogen fluoride solutions (contained in transparent Voltalef tubes 4-mm i.d.) or from mulls pressed between calcium fluoride windows, on a Cary 17 spectrophotometer.

The Raman spectra were recorded on a Coderg (Clichy, France) Model T800 spectrophotometer, using the 5145-Å exciting line from a Spectra Physics Model 164 argon laser. Solid samples were studied in sealed glass capillaries (0.5mm i.d) or in a spinning cell in order to reduce the decomposition of the sample by the laser beam. HF solutions were contained in transparent Voltalef tubes.

Accuracies of the measurements were ±1 cm^{-1} for Raman wavenumbers, ±5 cm^{-1} for infrared wavenumbers, and ±1 nm for the visible and near-infrared wavelengths.

Samples sealed in glass capillaries (~0.5-mm o.d) were used to obtain x-ray diffraction patterns on a Philips diffractometer (114-mm diameter). The exciting radiation was the copper Kα line (1.5418 Å).

ESR measurements were carried out with a Varian V4502-15 apparatus, at 77 K, the powdered sample being contained in a quartz tube, sealed under vacuum.

Enthalpimetric and thermal stability measurements were carried out on a microcalorimeter, Model MCB, from Arion Electronique (Grenoble, France). Powdered samples (100–200 mg) were contained in closed Monel cells and a heating rate of 2 K min^{-1} was used.

Chemical analyses were performed as follows. After hydrolysis of the sample, disproportionating U(V) into U(IV) and U(VI), uranium(VI) was determined by polarography in phosphoric acid–lithium perchlorate medium. A subsequent measurement, after oxidation of the sample by nitric acid, led to the total uranium content.

Fluorine was determined by pyrohydrolysis. The sample was heated to 1100 °C, and the evolved hydrogen fluoride was steam-extracted and collected in a sodium hydroxide solution. The fluoride ion concentration was then measured by absorptiometry of the alizarin–cerium complex at 617 nm.

The water content was determined by dissolving a known amount of sample in pyridine and titrating the evolved water with Karl Fischer reagent, using a Prolabo Aquavit titrator.

Preparation of $H_3O^+UF_6^-$. In a typical experiment, uranium pentafluoride (8.59 g, 25.8 mmol) was weighed into a 60-ml Voltalef flask in a drybox. This flask, fitted with a porous Teflon filter on the lid, was then transferred to the vacuum line and evacuated. A 25.8-mmol sample of twice-distilled water (464.3 mg) was weighed into another Voltalef flask which was cooled to −196 °C and carefully evacuated. Hydrogen fluoride (25 ml) was condensed into this vessel.