as a micro-crystalline precipitate, m.p. 165°, by addition of potassium iodide. The brown chloride is rapidly transformed in solution into the green salt. Heating on the water-bath soon transforms the brown iodide to the green iodide.

Anal. Calcd. for $Co(C_{22}H_{26}N_2O_2S_2)I.H_2O$: C, 42.7; H, 4.6; N, 4.5; Co, 9.5. Found: C, 42.5; H, 4.6; N, 4.6; Co, 9.6.

***d*-1,10-Bis-(salicylideneamino)-3,7-dithiadecane Cobalt-(III) *d*-Antimonyl Tartrate Dihydrate.**—The *dl*-iodide (green form) (3.2 g.) was suspended in water (40 ml.) at 80° and shaken with freshly precipitated silver chloride. After filtration the precipitate of silver halides was washed with a little dilute sodium nitrate solution in order to desorb adhering complex salt and the green filtrate evaporated rapidly to a volume of 40 ml. After removal of a small amount of tarry decomposition product potassium *d*-antimonyl tartrate (1.8 g.) in hot water (8 ml.) was added, the mixture cooled to room temperature and allowed to stand overnight. The crop of small brown plates which had separated was collected, the filtrate evaporated to about 30 ml., allowed to stand and a second crop of crystals obtained. The two crops were combined and recrystallized from hot water; minute brown plates which charred on heating being obtained.

Anal. Calcd. for $Co(C_{22}H_{26}N_2O_2S_2)(C_4H_4O_7Sb)\cdot 2H_2O$: N, 3.5; Sb, 15.3. Found: N, 3.5; Sb, 15.3.

A 0.02% aqueous solution at 20° (1-dm. tube) gave α_D +0.035°, whence $[\alpha]^{20}_D$ +1,750°.

***d*-1,10-Bis-(salicylideneamino)-3,7-dithiadecane Cobalt-(III) Iodide.**—The *d*-antimonyl tartrate just described was dissolved by grinding it (1 g.) with 10% sodium acetate solution (20 ml.). Solid potassium iodide was then added. The resulting brown amorphous precipitate of the *d* complex iodide was collected and washed with a little ice-water in which it is very soluble and then transformed to the chloride by shaking with freshly precipitated silver chloride and water (15 ml.). After removal of the silver halides the active iodide was obtained in crystalline form by gently warming, adding potassium iodide and scratching. The transformation to the chloride was necessary because of the tendency of the iodide to become tarry on warming with water. The crystalline solid was eventually recrystallized twice from methanol to which dry ether was added and obtained in micaceous plates, m.p. 234°.

Anal. Calcd. for $Co(C_{22}H_{26}N_2O_2S_2)I$: N, 4.7; Co, 9.8; I, 21.1. Found: N, 4.6; Co, 9.9; I, 21.4.

A 0.01% aqueous solution at 20° gave α_D +0.14° (1-dm. tube), and α_{5461} +0.11°, whence $[\alpha]^{20}_D$ +1,400°, $[\alpha]^{20}_{5461}$ +1,100°, $(M)^{20}_D$ +8,400° and $(M)^{20}_{5461}$ +6,600°.

***l*-1,10-Bis-(salicylideneamino)-3,7-dithiadecane Cobalt-(III) Iodide.**—The filtrate obtained from the precipitate of *d*-antimonyl tartrate mentioned above was fractionally precipitated with potassium iodide. The least soluble fractions were inactive but the more soluble were levorotatory. These were combined, transformed to the chloride with silver chloride and again fractionally precipitated, the process being repeated several times. The micaceous plates of the purified iodide eventually melted at 233°.

Anal. Found: N, 4.6; Co, 9.9; I, 21.3.

A 0.01% aqueous solution at 20° (1-dm. tube) gave α_D −0.13° and α_{5461} −0.10° whence $[\alpha]^{20}_D$ −1,300°, $[\alpha]^{20}_{5461}$ −1,000°, $(M)^{20}_D$ −7,800° and $(M)^{20}_{5461}$ −6,000°.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Inner Complexes of Uranium Containing 1,3-Dicarbonyl Chelating Groups

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In a search for moderately volatile uranium compounds, a series of uranyl and a series of uranium(IV) compounds of diketones and of ketoaldehydes were prepared. The data obtained indicate that the maximum attainable vapor tensions of uranium compounds of these types are unlikely to exceed 0.1 mm. at 130°. The preparation of the compounds investigated, the vapor tensions when large enough for measurement, and a few other properties are described.

Some time ago we undertook an investigation of complex compounds of uranium to ascertain whether among such substances there might be some having at least a moderate degree of volatility. After examination of the possibilities we decided to prepare a series of uranium compounds of the 1,3-diketone type. Thirteen such uranyl derivatives and ten derivatives of tetravalent uranium were prepared. Determination of their vapor tensions by measurement of the rate of effusion of their vapors[1] indicated to us that there is little likelihood of finding such compounds having vapor tensions much above 0.1 mm. at 130°. Furthermore the compounds most favorable from the point of view of volatility, *i.e.*, the derivatives of uranium(IV), had only a low degree of stability at temperatures at which the vapor tensions are appreciable.

Before this investigation was completed, uranium(IV) borohydride,[2] $U(BH_4)_4$, and its methyl derivatives[3] had been prepared, and had been found to have volatilities far higher than what appeared to be the maximum attainable volatility of the diketonates. For this reason the investigation of the latter type of compounds was discontinued.

It seems improbable that we shall return to this investigation. For this reason the following report of the results obtained is now presented.

Results and Discussion

Table I records the vapor tensions at 130°, and the melting points of a number of complex uranyl and uranium(IV) compounds. To save space the chelating agent is identified by formula only; the corresponding uranyl compounds have the formulas UO_2X_2, and the uranium(IV) compounds the formulas UX_4, in which X is the univalent negative ion of the chelating agent. A dash in column II means that the compound in question gave no indication of volatility, a zero that there was indication of volatility but that the vapor tension was too

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[1] M. Knudsen, *Ann. de. Physik*, **47**, 697 (1915); J. E. Mayer and I. H. Wintner, *J. Chem. Phys.*, **6**, 301 (1938).

[2] H. I. Schlesinger and Herbert C. Brown, THIS JOURNAL, **75**, 219 (1953).

[3] H. I. Schlesinger, H. C. Brown, L. Horvitz, A. C. Bond, L. D. Tuck and A. O. Walker, *ibid.*, **75**, 222 (1953).

TABLE I

MELTING POINTS AND VAPOR TENSIONS AT 130° OF INNER COMPLEXES OF URANIUM

	I	II Vapor tension × 10^{-2}, mm.		III M.p., °C.		IV % U		V
	Chelating agent	UO_2 der.	U(IV) der.	UO_2 der.	U(IV) der.	UO_2	U(IV) der.	Ref.
(1)	$CH_3COCH_2COCH_3$	..	0.91	225–250	175–176	50.38 (50.87)	38.54 (37.55)	*a*
(2)	$C_2H_5COCH_2COC_2H_5$	X	0.77	X	64–65	X	32.26 (31.91)	*b*
(3)	$CH_3COCH_2COC_2H_5$	0.0	2–4	206–208	59–60	47.33 (47.99)	36.50 (34.50)	*c*
(4)	$CH_3COCH_2COCH(CH_3)_2$	..	d.	112–115	Liq.	44.61 (45.43)	31.70 (31.90)	*d*
(5)	$CH_3COCH_2COCC(CH_3)_3$	..	1.9	150–152	d.	42.67 (43.12)	28.95 (29.68)	*e*
(6)	$CH_3COCH_2COC_6H_5$	..	d.	157–158	190–195	37.58 (40.71)	27.62 (26.99)	*f*
(7)	$CH_3COCH_2CO(C_4H_3O)$	..	0.0	172–175	195	39.94 (41.62)	26.44 (28.14)	*g*
(8)	CH_3COCH_2CHO	..	..	n.m.	n.m.	50.69 (54.10)	40.20 (41.19)	*h*
(9)	$C_6H_5COCH_2CHO$	..	d.	140–145	131–133 (d.)	43.51 (42.42)	28.71 (28.82)	*i*
(10)	$(CH_3)_3CCOCH_2CHO$	..	X	100	X	42.84 (45.43)	X	*j*
(11)	$CH_3COCH_2COCF_3$	0.27	8.0	199–200	138–140	41.38 (41.34)	28.56 (28.02)	*k*
(12)	$(CH_3)_3CCOCH_2COCF_3$	..	6.8	134–136	138	36.04 (36.08)	24.11 (23.39)	*k*
(13)	$CF_3COCH_2CO_2C_2H_5$	X	2.0	X	61	X	24.46 (24.48)	*l*

[a] C. E. Denoon, Jr., *Org. Syntheses*, **20**, 6 (1940). Both the $UO_2^=$ and the U(IV) derivatives had previously been prepared by W. Biltz and J. A. Clinch, *Z. anorg. Chem.*, **40**, 221 (1904). See also E. W. Abrahamson and A. S. Brown, THIS JOURNAL, **72**, 1424 (1950). [b] H. Fischer and E. Bartholamaus, *Ber.*, **45**, 1983 (1912). [c] G. T. Morgan and H. G. Reeves, *J. Chem. Soc.*, **123**, 447 (1923). [d] L. Claisen, *Ann.*, **277**, 168 (1893). [e] Same method as used for *a*. [f] L. Claisen, *Ann.*, **291**, 51 (1896). [g] J. M. Sprague, L. J. Beckham and H. Adkins, THIS JOURNAL, **56**, 2665 (1934). [h] Na salt, H. Gilman, private communication. [i] Na salt, A. Combes, *Compt. rend.*, **111**, 273 (1890). [j] F. Couturier and G. Vignon, *ibid.*, **140**, 1696 (1905). [k] To be described in Experimental part. [l] F. Swarts, *Bull. soc. acad. roy. Belg.*, [5] **12**, 679 (1926).

small for measurement at 130°, and a cross that the compound was not prepared. In column III the letters n.m. mean that the compounds behaved more like a typical salt than like an inner complex in that they failed to melt at temperatures comparable to those for the other compounds; the letter d. indicates that decomposition occurred at or below the temperature in question. To characterize the new uranium compounds, the observed uranium contents are given in column IV; the data in parentheses are the values calculated for the pure compound. The last column contains references from which the methods for preparing the chelating agents were taken. The method of preparation of the uranium salts is briefly described in the Experimental part.

The behavior of the following compounds toward uranyl nitrate and toward uranium(IV) chloride was also investigated: iminoacetylacetone, iminobenzoylacetone, glutaconic dialdehyde, ethyl acetoacetate, malonyl chloride and fluoride, diacetamide, dimethyl and diethyl malonates. All gave products which were unstable or extremely difficult to purify, or for other reasons made no contribution to the investigation.

The table shows that only two of the uranyl derivatives gave any indication of volatility at 130°, and that of these two only one had a vapor tension large enough for measurement by the effusion method employed. As is to be expected, the uranium(IV) compounds are invariably more volatile than the uranyl derivatives.

Reference to the table shows that replacement of both of the methyl radicals of acetylacetone by ethyl groups slightly decreased the vapor tension of the corresponding uranium(IV) compound. However, replacement of only one methyl group by an ethyl radical produced a nearly 3-fold increase in the 130° vapor tension. Decreasing the symmetry of the diketone molecule thus appears to increase the volatility of the complex, and this effect seems more pronounced than changes in the nature of the radicals replacing the methyl groups of the parent compound. This conclusion is borne out by the fact that compound 5 (the pivalylacetonate) has a volatility only slightly lower than compound 3 (the propionylacetonate).

Attempts further to increase the volatility of the uranium(IV) compounds by other alterations in what might be called the dissymmetry of the chelating molecule were unsuccessful. Thus replacement of one of the methyl groups by a phenyl radical led to a uranium complex of relatively low stability (compound 6), and replacement by an oxygen-containing radical resulted in a complex (compound 7) of vapor tension too low for measurement at 130°. Furthermore, ketoaldehyde complexes, which would have represented another type of dissymmetry, proved to be relatively unstable (compounds 8 and 9).[4]

A considerable increase in volatility was, however, achieved by replacing one of the methyl radicals of acetylacetone by the trifluoromethyl group as is shown by comparison of the vapor tension of compound 11 with that of compound 1. On the other hand, leaving the trifluoromethyl group unchanged, but replacing the remaining methyl by a pivalyl group (compound 12) produced a slight reduction of vapor tension, as was the case when the pivalyl group replaced the ethyl radical (compounds 3 and 5).

It is noticeable that replacement of the methyl groups of acetylacetone by ethyl groups greatly reduced the melting point of the derived uranium(IV) complexes, and that dissymmetry seemed somewhat to enhance this effect. Substitution of either chlorine atoms or methyl groups for the hydrogen of the 3-carbon atom markedly decreased the stability of the derived complexes. Likewise the derivatives of the ketoaldehydes studied were far less stable than those of the diketones. The presence of trifluoromethyl groups, on the other hand, not only seemed to increase the thermal stability of the derived compounds but greatly facilitated their preparation.

The number of compounds studied is too small for deducing general rules about the relationship of composition of the diketone to volatility, melting point and stability of the derived compounds. But, since replacement of methyl groups by larger radicals decreased the volatility, and their replacement by hydrogen atoms decreased the stability, the possible improvement due to dissymmetry must be sharply limited. It is upon these observations that we based our conclusion that a search for significantly more volatile uranium compounds of the diketone type held little promise of success.

Experimental

Measurement of Vapor Tensions.—For measurement of the vapor tensions by the effusion method,[1] the apparatus of Egerton[5] was used with very slight modification. The capsule from which effusion occurred was kept in contact with Woods metal to assure rapid attainment of thermal equilibrium. The apparatus was calibrated with dibutyl phthalate.

Preparation of the Diketones and Ketoaldehydes.—Except for two of the fluorine compounds, the diketones were prepared by methods described in the literature. Table I gives references from which the preparative methods were taken.

Preparation of 1,1,1-Trifluoropentane-2,4-dione, $CF_3COCH_2COCH_3$.—A mixture of 3.8 g. of sodium (powdered under 80 cc. of xylene) and 9.5 cc. of ethanol was heated until only a small amount of the metal was left. The resulting solution was cooled, and treated with a solution of 23.0 g. of ethyl trifluoroacetate[6] in 11.9 cc. of acetone, during which procedure the temperature rose to 65°. The dark reddish-brown solution, which had formed after 1.5 hours, was heated for 2 hours on the steam-bath, and then was allowed to stand overnight before it was poured into water. The water-insoluble layer was extracted three times with water. The aqueous solution was acidified with sulfuric acid, and treated with copper acetate. The mixture was allowed to stand at 0° to allow complete precipitation of the copper salt. The latter (23 g.), while still damp, was dissolved in 50 cc. of ether and treated with 75 cc. of 20% sulfuric acid. Continued, vigorous shaking of the mixture was required to complete decomposition of the salt. After several ether extractions of the water layer, the combined ethereal solutions were dried over sodium sulfate. The ether was removed through an efficient column. The residue was fractionated, giving a 38% yield of the diketone boiling at 79–81°. The copper salt, which had been recrystallized from aqueous methanol, and which melted at 190–192°, was analyzed.

Anal. Calcd.: Cu, 17.05. Found: Cu, 17.7.

Preparation of 1,1,1-Trifluoro-5,5-dimethylhexane-2,4-dione, $CF_3COCH_2COC(CH_3)_3$.—The compound was prepared in analogous fashion, except that after the addition of ethyl trifluoroacetate, 16.2 g. of pinacolone, instead of acetone, was added in small portions. The yield was 59% of material boiling at 138–141°. The copper salt melted at 108–110°.

Anal. Calcd.: Cu, 13.95. Found: Cu, 14.14.

Analysis of the Uranium Compounds.—For analysis, the uranium compounds were dissolved in concentrated nitric acid. The resulting solutions were boiled until evolution of oxides of nitrogen ceased, and were then evaporated to dryness. The procedure was repeated several times to ensure complete oxidation of organic material and complete conversion of uranium(IV) to uranyl nitrate. The residue was taken up in water and analyzed for uranium by the 8-hydroxyquinoline method. The results tended to be slightly high.

Preparation of the Uranium Complexes.—The compounds were prepared by adding the diketone or its aqueous solution to an aqueous solution of the uranyl salt (usually the nitrate) or to an aqueous solution of uranium(IV) chloride. In general, the desired compounds did not precipitate until the acidity of the reaction mixture had been decreased by the addition of aqueous sodium hydroxide. Too much of the latter causes contamination of the desired products with uranium hydroxides. Shaking or stirring of the mixtures during the addition of the base, to avoid local excesses, and discontinuance of the addition at between *p*H 4 and 6, are essential. In the preparation of the uranium salts of the ketoaldehydes aqueous solutions of the sodium salts of the latter, made barely acid with acetic acid, were used; in these cases addition of sodium hydroxide was not necessary.

The uranyl complexes were more easily obtained in satisfactory condition than were the uranium(IV) complexes. The initial precipitates of the former, though usually crystalline, were occasionally gummy; the gummy masses, however, crystallized either on standing or on purification of the crude product. Purification was effected by recrystallization from methanol or from ethanol, or by dissolving the crude product in the one or the other of these alcohols and bringing about reprecipitation by the addition of water.[7]

The uranium(IV) derivatives are less stable and more easily hydrolyzed than the uranyl derivatives, and are, in addition, readily oxidized by air. Furthermore, the crude materials very frequently were oils rather than solids. To obtain satisfactory products all manipulations were carried out as rapidly as possible, and with minimum exposure of the products to air. Particular care was necessary not to exceed the optimum amount of base. When the crude product was a solid, its recrystallization from absolute methanol, followed by removal of the solvent from the crystals in vacuum, sufficed for purification. When the crude product was an oil, it was extracted with ether. If removal of the latter from the dried solution again left an oil, purification was effected by molecular distillation at 115–130° and 10^{-4} mm.; a solid residue after ether removal, was dissolved in ligroin and reprecipitated by cooling the solution to -80°. It should be mentioned that the fluorine-containing compounds were less difficult to purify than the others.

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(4) It may be mentioned that replacement of the central hydrogen atom of the diketone by a chlorine atom or a methyl group led to the formation of less volatile, as well as less stable, complexes.

(5) A. C. Egerton, *Proc. Roy. Soc.*, **A103**, 469 (1923).

(6) A. L. Henne, T. Alderson and M. S. Newman, THIS JOURNAL, **67**, 918 (1945).

(7) The uranyl acetylacetonate was recrystallized from ethylene dichloride.