938. *The Chemistry of Uranyl Acetylacetone Complex.*

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Three crystalline modifications of uranyl acetylacetone monohydrate have been prepared and their unit-cell parameters, infrared spectra, visible spectra, and magnetic susceptibilities studied. Crystalline solvates of uranyl acetylacetone have also been prepared with ethanol, dioxan, acetylacetone, and acetophenone.

The visible and ultraviolet spectra of solutions of anhydrous uranyl acetylacetone in ethanol and in benzene are presented; the compound is dimeric in benzene at 80°.

The electrical conductivities of aqueous solutions of uranyl acetylacetone have been measured: at 0·2° the solutions are relatively stable and the equivalent conductivity is approximately unity at 10^{-4}M; at 25° the solutions are rapidly hydrolysed with deposition of $UO_3,2H_2O$.

Many co-ordination compounds of the uranyl ion have been prepared,[1] but none has been studied in sufficient detail to enable even the co-ordination number of the uranium atom to be determined. The visible and ultraviolet absorption spectra of solutions of the uranyl complexes of several aromatic β-diketones have been examined by Sacconi and Giannoni,[2] who conclude that in these compounds the co-ordination number of the uranium atoms exceeds six. Uranyl acetylacetone monohydrate was prepared first by Biltz and Clinch,[3] and more recently by Gilman and his co-workers.[4] Abrahamson and Brown [5] and Schlesinger and his co-workers [6] have prepared the anhydrous compound.

We prepared uranyl acetylacetone monohydrate by the slow addition of aqueous sodium hydroxide to warm aqueous solutions containing equivalent quantities of uranyl nitrate and acetylacetone. The crystals which formed when these solutions cooled under apparently identical conditions assumed a wide variety of habits; seeding was of major importance. They were examined by optical and *X*-ray crystallography and had three main crystalline forms, two of which (forms 1 and 2) were yellow and one (form 3) was red. Photographs of typical preparations are given in the Plate.

Form 3 was unstable, changing spontaneously into form 2. Some preparations of form 3 started to change colour within a few hours of preparation, whereas one was still unchanged after two years: samples kept at *ca.* 4° remained unchanged indefinitely. Observations with a polarising microscope showed that when a red crystal had changed into the yellow form the shape was at first unchanged but the " crystal " was granular and microcrystalline. After several months at room temperature the " crystal " became macrocrystalline and the outline was distorted by the new crystal faces. In one preparation there was no distortion of the crystals; they slowly changed into yellow single crystals while maintaining their original form, but they now showed oblique extinction. Oscillation photographs of one of these new yellow crystals showed it to be of form 2, and this was also shown by *X*-ray powder photographs and the infrared spectrum of this material.

Crystals of form 1 became opaque on long exposure to the atmosphere, and *X*-ray powder photographs showed that they had changed into $UO_3,2H_2O$.

When crystals of form 3 were immersed in dichloroethane at room temperature they dissolved, crystals of form 1 being formed simultaneously. When the dichloroethane was initially saturated with respect to form 1 these new crystals developed on the faces of the

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[1] Croxton, " Uranium and its Compounds; a Bibliography of Unclassified Literature," U.S.A.E.C. report K-295, part 2 (1951); Allen, supplement to same. T.I.D. 3041 (1953); Comyns, " The Co-ordination Chemistry of Uranium: a Critical Review," A.E.R.E. report C/R 2320 (1957).

[2] Sacconi and Giannoni, *J.*, 1954, 2368, 2751.

[3] Biltz and Clinch, *Z. anorg. Chem.*, 1904, **40**, 218.

[4] Gilman, Jones, Bindschadler, Blume, Karmas, Martin, Nobis, Thirtle, Yale, and Yoeman, *J. Amer. Chem. Soc.*, 1956, **78**, 2790.

[5] Abrahamson and Brown, *ibid.*, 1950, **72**, 1424.

[6] Schlesinger, Brown, Katz, Archer, and Lad, *ibid.*, 1953, **75**, 2446.

form 3 crystals; this process is shown in the Plate. Recrystallisation of crystals of form 1 from warm dichloroethane gave well-developed crystals of form 1, although some precipitation of a hydrolysis product (probably $UO_3,2H_2O$) occurred if the solution was kept warm for too long.

Crystal Data.—*Form* 1. Two closely-related modifications of this form occurred together, both in batches prepared from aqueous solution and in those crystallised from dichloroethane. Form 1*A* is orthorhombic, elongated along [010], with $a = 16{\cdot}72 \pm 0{\cdot}05$, $b = 7{\cdot}06 \pm 0{\cdot}01$, $c = 48{\cdot}5 \pm 0{\cdot}1$ Å. The calculated density, 16 molecules being assumed per unit-cell, is 2·26 g./c.c. Form 1*B* is monoclinic, elongated along [010], with $a = 16{\cdot}64 \pm 0{\cdot}05$, $b = 7{\cdot}06 \pm 0{\cdot}01$, $c = 12{\cdot}92 \pm 0{\cdot}05$ Å, $\beta = 109{\cdot}0° \pm 0{\cdot}5°$. The calculated density, 4 molecules being assumed per unit-cell, is 2·25 g./c.c. The observed density, for a sample consisting of a mixture of both forms, was 2·26 g./c.c. The geometrical relation between the two unit-cells is approximately as shown in Fig. 1, but careful comparison of the two modifications showed that the spacing along [001] in form *A* is less than four times that in form *B*.

FIG. 1. *Relation between the orthorhombic unit-cell of form* 1*A*, *and the monoclinic unit-cell of form* 1*B*. *The a-dimensions (not shown) are identical.*

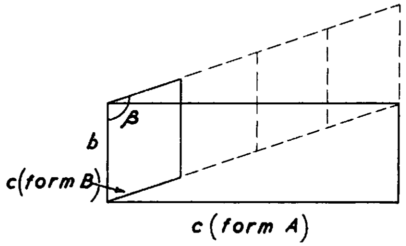
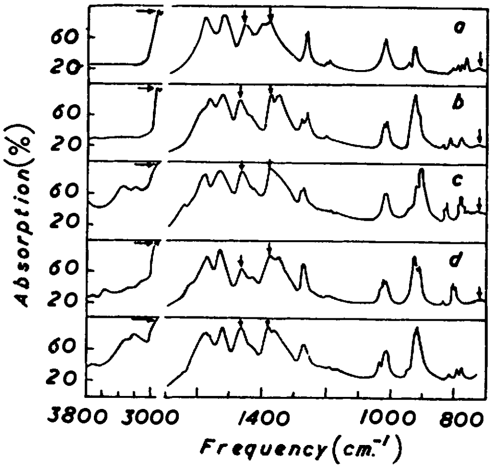


FIG. 2. *Infrared spectra of thorium and uranyl acetylacetones.*



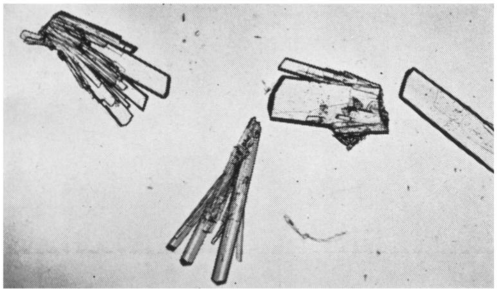
a, $Th(C_5H_7O_2)_4$; *b*, $UO_2(C_5H_7O_2)_2$;
c, $UO_2(C_5H_7O_2)_2,H_2O$, form 3;
d, $UO_2(C_5H_7O_2),H_2O$, form 2;
e, $UO_2(C_5H_7O_2),H_2O$, form 1.
Nujol bands are marked by arrows.

In form 1*B* all *X*-ray reflections of the class *hkl* with *l* odd were observed as streaks rather than spots. This indicates a disordered structure, which will be described in detail elsewhere.

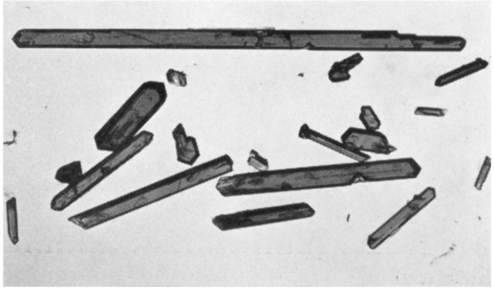
Form 2. Two monoclinic habits were observed: rectangular tablets, elongated along [010], showing straight extinction; and prisms, elongated along [100], with oblique extinction: the optic sign was negative. The cell-dimensions were: $a = 7{\cdot}825 \pm 0{\cdot}010$, $b = 11{\cdot}98 \pm 0{\cdot}01$, $c = 15{\cdot}65 \pm 0{\cdot}02$ Å, $\beta = 103{\cdot}7° \pm 0{\cdot}3°$, and the space-group $P2_1/c$. The calculated density, 4 molecules being assumed per unit-cell, is 2·27 g./c.c.; that observed was 2·24 g./c.c.

Form 3. This occurred as orthorhombic red needles, elongated along [001], showing straight extinction: the optic sign was negative. The cell-dimensions were: $a = 25{\cdot}46 \pm 0{\cdot}10$, $b = 12{\cdot}95 \pm 0{\cdot}05$, $c = 8{\cdot}92 \pm 0{\cdot}05$ Å, and the space-group *Pccn*. The calculated density, 8 molecules being assumed per unit-cell, is 2·20 g./c.c.; that observed was 2·22 g./c.c.

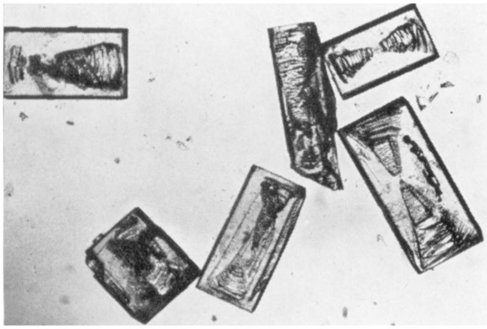
Infrared Spectra.—Infrared spectra of the three monohydrates and the anhydrous



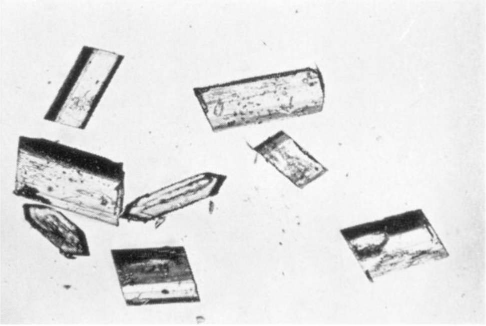
Form **1** (× 18)



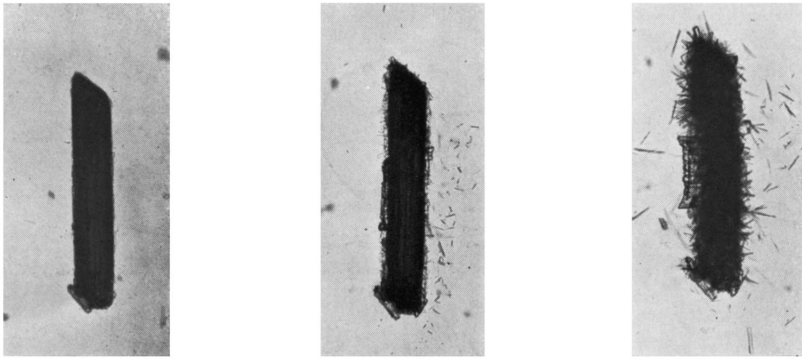
Form **3** (× 23)



Form 2 (× 20)



Form 2 (× 20)



(*a*) (*b*) (*c*)

Form **3** (× 23) in saturated dichloroethane:

(*a*) After $\frac{1}{2}$ min. (*b*) After 2 min. (*c*) After 18 min.

Crystals of uranyl acetylacetone monohydrate.

form of uranyl acetylacetone, and of thorium acetylacetone, are shown in Fig. 2, and the frequencies of the bands are given in the Table. No absorption band was observed between 2860 and 1700 cm.$^{-1}$. The spectra of the anhydrous forms derived from all three monohydrates were almost identical. The spectrum of the yellow monohydrate obtained by spontaneous transformation of the red monohydrate (form 3) at room temperature was found to be almost identical with that of the monohydrate of form 2.

Bands due to water. Thorium acetylacetone and anhydrous uranyl acetylacetone showed no absorption band in the 3000 cm.$^{-1}$ or the 1640 cm.$^{-1}$ region. All three monohydrates of uranyl acetylacetone exhibited a shoulder or a peak at *ca.* 1640 cm.$^{-1}$, characteristic of the bending vibration of the water molecule, and also a pair of broad bands in the region 3000—3400 cm.$^{-1}$, characteristic of the two stretching vibrations of the water molecule. In addition, form 2 of the monohydrate exhibited a weak but sharp peak at 3580 cm.$^{-1}$. This peak could be due to hydroxyl groups either attached to uranium or in the form of enolic acetylacetone, but it is more probably due to a complex splitting of the O–H stretching vibrations of water molecules. Similar spectra in this region are given by some hydrated metal halides [7] and by hydrated cyclic metaphosphates.[8]

Infrared absorption frequencies of uranyl and thorium acetylacetones.

Uranyl acetylacetone							Thorium acetylacetone
Form 1 hydrate	Form 2 hydrate	Form 3 hydrate	Form 3 trans.	Form 1 anhyd.	Form 2 anhyd.	Form 3 anhyd.	
		761					765
		(774)					
780		781		777	778	778	779
793	799		799				792
	805		805				805
814				816	816	816	
		825					
	835	830	836	837	838	837	
					(903)		
	912	918	910	(912)	(910)	914	923
917	925	905	924	924	925	926	
(943)		(942)	(947)				943
1012	1014	1017	1014	1012	1014	1019	1018
	1024		1022	1022	1024	1024	
(1032)	(1031)		(1032)				
		1176	1171	1172		1172	
1195	1198	1190	1200	1200	1200	1200	1193
1271	1272	1272	1276	1264	1264	1264	1267
		(1280)		1279	1277	1279	
1361	1348	(1370)	1348	1350	1351	1351	1401
(1431)	1427	1431	1433	(1437)	(1437)	1435	
1524	1531	1534	1531	1531	1529	1529	1531
1572	1572	1580	1577	1575	1570	1567	1585
1577							
				1592	(1590)	(1590)	
(1650)	(1637)	1647	1639				
3205	(3090)	3205	×				
(3320)	3255	3362	×				
	3580		×				

Units, cm.$^{-1}$. Approximate positions of shoulders are given in parentheses. Regions marked × were not examined with the lithium fluoride prism. " Form 3 trans." denotes a sample of the form 3 monohydrate which had spontaneously transformed into a yellow form at room temperature.

Bands due to the uranyl ion. The strongest band in the region 900—950 cm.$^{-1}$ in the spectra of the uranyl acetylacetones is assigned to the asymmetric stretching frequency of the uranyl ion. In other crystalline uranyl compounds this vibration has been found [9]

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[7] Duval and Lecomte, *J. Chim. phys.*, 1953, **50**, 64.

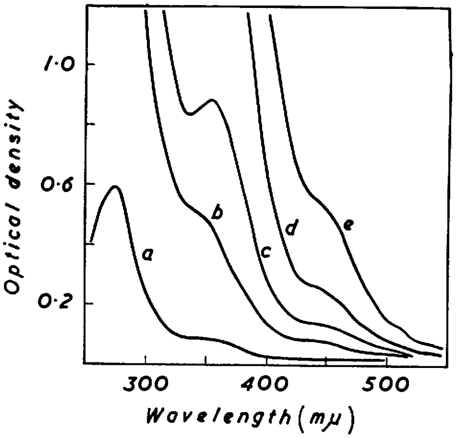
[8] Corbridge and Lowe, *J.*, 1954, 493.

[9] Conn and Wu, *Trans. Faraday Soc.*, 1938, **34**, 1483; Lecomte and Freymann, *Bull. Soc. chim. France*, 1941, **8**, 622; Sevchenko and Stepanov, *Zhur. eksp. teor. Fiz.*, 1949, **19**, 1113 (A.E.R.E. translation No. 11/3/5/80); Jones, *J. Chem. Phys.*, 1955, **23**, 2105; Gatehouse and Comyns, unpublished work.

between 909 and 950 cm.$^{-1}$, typically near 920 cm.$^{-1}$. In forms 1 and 2 of uranyl acetylacetone monohydrate and in the anhydrous compound the frequencies are also in this range, but in form 3 of the monohydrate the frequency has the unusually low value of 905 cm.$^{-1}$. This probably reflects some abnormality in the structure of the uranyl ion in this form, which is also responsible for the abnormal colour.

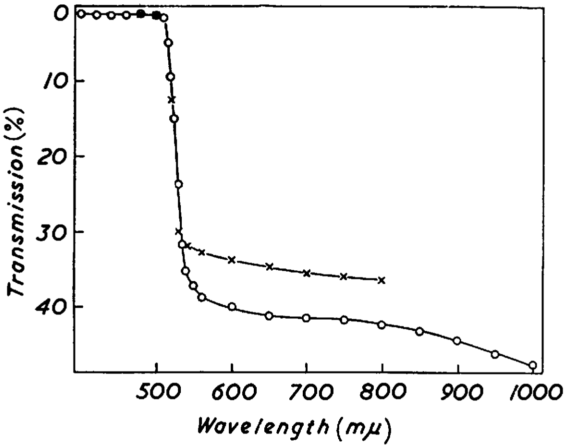
Bands due to the acetylacetone radical. Several studies have been made of the infrared spectra of acetylacetone and its metal derivatives,[10, 11] and a fairly complete frequency assignment has been made by Lecomte and his co-workers.[11] Morgan [12] has reported the infrared spectrum of thorium acetylacetone, but his figure and table of frequencies are not self-consistent and both differ in many respects from the spectrum presented here.

FIG. 3. *Absorption spectra of uranyl acetylacetone solutions.*



a, c, e, in ethanol, in 10 cm. cell, 3·60 × 10^{-6}, 3·60 × 10^{-5}, and 1·80 × 10^{-4}M respectively; *b, d,* in benzene, in 1 cm. cell, 1·85 × 10^{-4} and 9·23 × 10^{-4}M respectively.

FIG. 4. *Absorption spectrum of uranyl acetylacetone monohydrate, form* 1.



○ At 25°. × At −196°.

When the spectra of the uranyl acetylacetones are compared with those of other metal acetylacetones between 1300 and 850 cm.$^{-1}$ (where skeletal vibrations occur) the bands in the uranyl spectra are found in the same regions but are more complex. These splittings of the skeletal bands probably result from interactions between neighbouring acetylacetone radicals.

Visible and Ultraviolet Spectra of Solutions.—Absorption spectra of solutions of anhydrous uranyl acetylacetone in ethanol and in benzene at room temperature are shown in Fig. 3. The ethanolic solutions exhibit an intense peak at 272 mμ (ε 16,400), a peak or shoulder at 353 mμ (ε 2500), a weak shoulder at 448 mμ (ε ≏ 280), and a very weak shoulder at 510 mμ (ε ≏ 60). The spectra of the benzene solutions are similar, but observations in this solvent could not be made below 300 mμ. The solutions did not fluoresce in ultraviolet light at room temperature.

The bands at 272 and 353 mμ resemble those reported for uranyl trifluoroacetylacetone

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[10] Lecomte and Freymann, *Compt. rend.*, 1939, **208**, 1401; Kahovec and Kohlrausch, *Ber.*, 1940, **73**, 1304; Lecomte, *Discuss. Faraday Soc.*, 1950, **9**, 125; Bellamy, Spicer, and Strickland, *J.*, 1952, 4653; Shigorin, *Izvest. Akad. Nauk S.S.S.R., ser. Fiz.*, 1953, **17**, 596; *Idem, Zhur. fiz. Khim.*, 1953, **27**, 554; Bellamy and Branch, *J.*, 1954, 4491; Belford, Martell, and Calvin, *J. Inorg. Nuclear Chem.*, 1956, **2**, 11; Mecke and Funck, *Z. Elektrochem.*, 1956, **60**, 1124; Holtzclaw and Collman, *J. Amer. Chem. Soc.*, 1957, **79**, 3318; West and Riley, *J. Inorg. Nuclear Chem.*, 1958, **5**, 295.

[11] Duval, Freymann, and Lecomte, *Compt. rend.*, 1950, **231**, 272; *idem, Bull. Soc. chim. France*, 1952, **19**, 106.

[12] Morgan, U.S.A.E.C. report AECD-2659 (1949).

by Haszeldine and his co-workers[13] and for uranyl benzoylacetone by Sacconi and Giannoni.[2] The two weak bands, if present in the spectra of these compounds, would probably not have been observed by these workers at the concentrations they employed.

The spectra of the metal acetylacetones were studied by Sone and his co-workers[14] and by Kiss,[15] who found from 1 to 3 bands in the ultraviolet region (in Kiss's terminology, bands *d*, *e*, and *f*) due to transitions in the ligand, and bands in the visible and ultraviolet regions due to transitions in the metal ion modified by the ligand. The bands in the uranyl acetylacetone spectra at 272 and 353 mμ are clearly assignable to Kiss's bands *e* and *d* respectively. The 448 mμ band, from its position and low intensity, is almost certainly a modified form of the uranyl band. The 510 mμ band may also be due to the uranyl ion, although it falls just outside the range of bands usually observed in the spectra of uranyl ions in solution.[16]

Sacconi and Giannoni[2] assigned the bands in their spectra at 376—403 mμ to the uranyl ion, but the occurrence of these bands in the spectra of the acetylacetones of other metals, their strong intensities, and the present discovery of a band at 448 mμ, make this assignment improbable.

The solutions in benzene, as well as in other non-co-ordinating solvents including chlorobenzene and dichloroethane, become redder on heating, whereas solutions in co-ordinating solvents including ethanol, *n*-pentyl acetate, and *cyclo*hexanone do not. Anomalously, chloroform solutions do not change colour. This effect was not studied spectrophotometrically, but may result from a small broadening of the absorption bands with increasing temperature.[17]

The molecular weight of anhydrous uranyl acetylacetone in benzene at 80° corresponds with that of a dimer.

Visible Spectra of Crystals.—The visible absorption spectra of single crystals of the red (form 3) and one of the yellow (form 1) monohydrate of uranyl acetylacetone, measured at room and liquid nitrogen temperatures, are shown in Figs. 4 and 5. To examine the pleiochroism, the spectrum of the red form was obtained with polarised light.

The yellow form exhibited a sharp step at 510—540 mμ, and the red form a similar but less steep one at 550—600 mμ. At shorter wavelengths than these steps, where the uranyl absorption bands are normally found, no light was transmitted through the crystals because they were too thick. At longer wavelengths there were no absorption bands: less light was transmitted in this region at low temperatures than at high, probably owing to variation of the refractive index with temperature which would vary the ratio of transmitted to reflected light.*

The wavelength of the step in the spectrum of the yellow form corresponds with that of the resonance line observed in the absorption spectra of other crystalline uranyl compounds.[18] The step in the spectrum of the red form probably corresponds with the resonance line of a different electronic transition.

Crystals of uranyl acetylacetone monohydrate, form 1, showed a strong yellow fluorescence, and form 2 a weak yellow fluorescence, in ultraviolet light at −196° but not at +25°. Crystals of the monohydrate, form 3, and the anhydrous form, did not fluoresce. Thorium acetylacetone gave a white fluorescence at −196° but not at +25°.

Magnetic Susceptibilities.—Magnetic susceptibilities of the three monohydrates of

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* We are grateful to Dr. G. T. Rogers for this suggestion.

[13] Haszeldine, Musgrave, Smith, and Turton, *J.*, 1951, 609.

[14] Sone, Miyake, Kuroya, and Yamasaki, *J. Chem. Soc. Japan*, 1948, **69**, 70; Yamasaki and Sone, *Nature*, 1950, **166**, 998; Sone, *J. Amer. Chem. Soc.*, 1953, **75**, 5207.

[15] Kiss, *Magyar Tud. Akad. Kém. Tud. Oszt. Közl.*, 1957, **9**, 257; Kiss and Császár, *Acta Chim. Acad. Sci. Hung.*, 1957, **13**, 49.

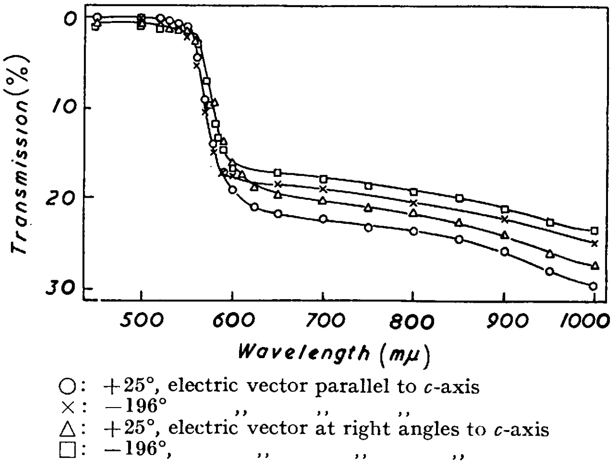
[16] Rabinowitch, " Absorption Spectra of Uranyl Compounds in Solution," U.S.A.E.C. report ANL-5173 (1953).

[17] Grubb and Kistiakowsky, *J. Amer. Chem. Soc.*, 1950, **72**, 419.

[18] Rabinowitch, " Spectroscopy of Uranyl Salts in the Solid State," U.S.A.E.C. report ANL-5122 1953).

uranyl acetylacetone and a dehydrated sample of the form 1 monohydrate were measured at 25°. A Gouy balance was used, calibrated by $CuSO_4,5H_2O$. The materials were all weakly diamagnetic, values for χ_m ranging from -52×10^{-6} to -106×10^{-6} c.g.s. units. The susceptibility calculated for $UO_2(C_5H_7O_2)_2,H_2O$ is $\chi_m = -54 \times 10^{-6}$ on assumed $\chi_m$values for the uranyl ion[19] of $+57 \times 10^{-6}$, for water[20] of -13×10^{-6}, and for the acetylacetone ion[21] of -49×10^{-6} c.g.s. units. Deviations between the individual experimental values, and between these and the calculated value, are within experimental error. There is thus no major difference between the magnetic properties of the uranyl ions in these compounds.

FIG. 5. *Absorption spectrum of uranyl acetylacetone monohydrate, form* 3.



○: +25°, electric vector parallel to c-axis
×: −196° ,, ,, ,,
△: +25°, electric vector at right angles to c-axis
□: −196°, ,, ,, ,,

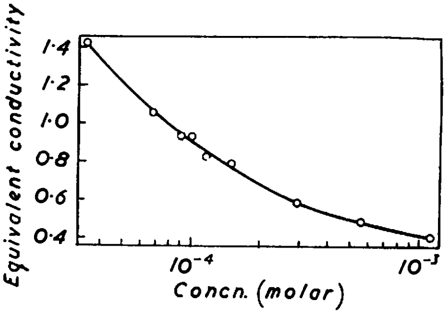


FIG. 6. *Equivalent conductivity of uranyl acetylacetone at* 0·2°.

Electrical Conductivities.—When uranyl acetylacetone monohydrate was added to conductivity water at 25° the conductivity rose as the crystals dissolved, and then fell rapidly. After about 20 min. the solution was opalescent and in a few hours a precipitate of $UO_3,2H_2O$ formed.

When the experiment was performed at 0·2° the conductivity rose as the crystals dissolved, and when they had all dissolved it continued to rise but much more slowly. This second rise was linear for several hours, and extrapolation to the time of addition of the crystals gave an approximate value for the equivalent conductivity of the solution before the onset of the process responsible for the second rise. The variation with concentration of the extrapolated conductivity at 0·2° is shown in Fig. 6. Extrapolation of the curves obtained at 25° was impossible, but the conductivities at the maxima of the curves

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[19] Freed and Kasper, *J. Amer. Chem. Soc.*, 1930, **52**, 4671; Lawrence, *ibid.*, 1934, **56**, 776.
[20] Selwood, " Magnetochemistry," Interscience, New York, 1956, p. 85.
[21] Hutchison and Elliott, *J. Chem. Phys.*, 1948, **16**, 920.

at concentrations between 4×10^{-5} and 2×10^{-4}M were about three times as great as the extrapolated conductivities at corresponding concentrations at 0·2°.

From the work of Rydberg[22] and of Fernelius and his co-workers[23] it is reasonable to assume that the following two equilibria are responsible for the extrapolated conductivities at 0·2°:

$$\mathrm{UO_2\,Acac_2} \rightleftharpoons \mathrm{UO_2\,Acac^+} + \mathrm{Acac^-}$$
$$\mathrm{UO_2\,Acac^+} \rightleftharpoons \mathrm{UO_2^{++}} + \mathrm{Acac^-}.$$

The cause of the slow rise in conductivity at 0·2° is obscure.

At 25° the net reaction is

$$\mathrm{UO_2\,Acac_2} + 3\mathrm{H_2O} = \mathrm{UO_3,2H_2O} + 2\mathrm{H\,Acac}$$

Probably the two reactions postulated at 0·2° occur immediately on dissolving the crystals in water, and these are followed by a succession of hydrolytic steps which reduce the conductivity essentially to that of aqueous acetylacetone. The uranyl ion is known to be extensively hydrolysed[24] in solutions of $\mathrm{pH} > 3$, and although the pH values of the very dilute solutions of the complexes were not measured they must have exceeded this.

Reactions.—In common with other uranyl diketone complexes,[2] uranyl acetylacetone forms an addition compound with pyridine,[25] and double salts of the type $\mathrm{R^+\,[UO_2(C_5H_7O_2)_3]^-}$ (where $\mathrm{R^+ = NH_4^+}$, $\mathrm{CH_3{\cdot}NH_3^+}$, $\mathrm{C_6H_5{\cdot}NH_3^+}$) have also been described.[25]

When uranyl acetylacetone is crystallised from co-ordinating organic solvents, the product is usually solvated. Solvates with ethanol, dioxan, acetylacetone, and acetophenone have now been prepared, all of which contain one molecule of solvent to each uranium atom.

When an attempt was made to prepare a uranyl acetylacetone perchlorate analogous with the compound $\mathrm{Mn(C_5H_7O_2)_2,ClO_4(H_2O)_2}$ described by Cartledge,[26] by triturating uranyl acetylacetone monohydrate with perchloric acid, the product was identical with the solvate obtained by crystallising uranyl acetylacetone from acetylacetone. Evidently some of the uranyl complex is decomposed with liberation of free acetylacetone, which then combines with the remainder of the complex.

The monohydrates of uranyl acetylacetone are readily dehydrated at 100° under vacuum, the crystals falling to an orange powder. The anhydrous forms yielded by the three monohydrates gave almost identical infrared spectra. Contrary to Abrahamson and Brown's observations,[5] the anhydrous material took up water only very slowly on exposure to the atmosphere. The anhydrous material can be crystallised from dichloroethane[6] or from chlorobenzene: in both cases precautions must be taken to exclude moisture, or the monohydrate (form 1) is produced.

DISCUSSION

That uranyl acetylacetone cannot be represented by the simple formula (I) is shown by the ebullioscopic measurements. The dimeric molecules in benzene may be held together in one of several ways: by acetylacetone bridges, by co-ordination of the uranyl oxygen atoms to the adjacent uranium atoms, or by co-ordination of the acetylacetone oxygen atoms to the adjacent uranium atoms. The third possibility seems the most likely; if only one oxygen atom from each molecule were co-ordinated in this way then

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[22] Rydberg, *Arkiv Kemi*, 1955, **8**, 113; *idem*, *Svensk kem. Tidskr.*, 1955, **67**, 499.

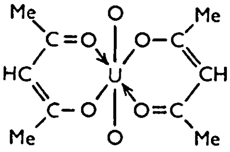
[23] Izatt, Fernelius, and Block, *J. Phys. Chem.*, 1955, **59**, 80; and other papers in this series.

[24] Sutton, *J.*, 1949, S275; Ahrland, *Acta Chem. Scand.*, 1949, **3**, 374; Ahrland, Hietanen, and Sillén, *ibid.*, 1954, **8**, 1907; Hearne and White, *J.*, 1957, 2168.

[25] Hager, *Z. anorg. Chem.*, 1927, **162**, 82.

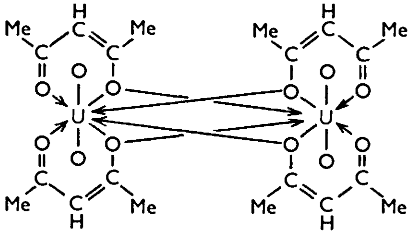
[26] Cartledge, *J. Amer. Chem. Soc.*, 1952, **74**, 6015.

the uranium atoms would have a co-ordination number of seven, and if two were co-ordinated the co-ordination number would be eight. The latter possibility is shown diagrammatically in (II), no assumptions being made about the nature of the bonds.



(I)

(II)



The molecular complexity in co-ordinating solvents may well be less than in benzene, since co-ordination by solvent molecules is probably easier sterically than co-ordination of type (II): both processes could, however, occur together. The involatility of anhydrous uranyl acetylacetone [4,6] suggests that the molecules are polymerised in the crystal as well as in benzene solution.

The cause of the unusual colour of the monohydrate, form 3, is obscure; perhaps the configuration of the atoms surrounding the uranyl ions, or the co-ordination number of the uranium atoms, is unusual. The uranyl ions must have substantially the same structure in all the monohydrates since, if the ions were bent, the symmetric stretching frequency would appear in the infrared spectrum, and if any other atoms were attached through the uranyl oxygen atoms then the asymmetric stretching frequency would be markedly shifted. The small decrease in the asymmetric stretching frequency observed in the red monohydrate may be due to a small lengthening of the U–O bonds.

EXPERIMENTAL

Acetylacetone (B.D.H.) was dried (K_2CO_3) and fractionated in a Widmer column, b. p. 132—134°. Dichloroethane (Tyrer) was shaken with water to remove acid, and dried (Na_2SO_4).

Analyses for uranium were made by ignition to 750—850° for several hours and weighing the residual U_3O_8. Some commercial carbon and hydrogen analyses were made, but the results were unreliable.

Probably all the hydrates, other than that made by crystallisation from dichloroethane, were slightly contaminated by $UO_3,2H_2O$. Crystals of all three forms, when dissolved in alcohol or dichloroethane on a microscope slide, left faint ' ghosts ' of minute insoluble particles. This contamination was probably responsible for the small variation in uranium content observed between different batches of the same form.

Preparations.—Form 1. This was the most commonly obtained form. Sodium hydroxide solution (3·0N) was added dropwise to a solution of uranyl nitrate hexahydrate (10·0 g.) and acetylacetone (4·0 ml.) in water (30 ml.) at 80°. Crystallisation started when 9 ml. of alkali had been added, and the mixture was then allowed to cool slowly to room temperature. The crystals (form 1) were filtered off, yield 6·8 g. [Found: U, 48·87, 48·88, 48·99. Calc. for $UO_2(C_5H_7O_2)_2,H_2O$: U, 48·97%].

Crystals of form 1 (10 g.) from a similar, larger preparation were crystallised from dichloroethane (60 ml.), the hot solution being first decanted from a small amount of yellow solid. The crystals, also of form 1, were filtered off, yield 8·2 g. (Found: U, 48·88, 48·85, 48·85, 48·84%). A portion was dehydrated over P_2O_5 for 5 hours at 100°/0·02 mm. and gave a fine orange powder [Found: U, 50·69, 50·70, 50·59, 50·67. Calc. for $UO_2(C_5H_7O_2)_2$: U, 50·85%].

Form 2. When almost any preparation was filtered before crystallisation was complete, the crystals deposited by the filtrate were of form 2. Crystals so obtained were ground between glass slides, and the powder was used to seed a preparation similar to one which usually gave form 1 in the absence of seeding.

Sodium hydroxide solution (16 ml., 3·0N) was added slowly to a solution of uranyl nitrate hexahydrate (20·0 g.) and acetylacetone (8 ml.) in water (200 ml.) at 75°. The solution was seeded and allowed to cool slowly. The crystals (form 2) were filtered off, yield 6·5 g. (Found: U, 49·19, 49·29, 49·22%). A portion was dehydrated (over P_2O_5) for 6 hr. at 100°/0·02 mm. and gave a fine orange powder (Found: U, 51·13, 50·62, 50·63%).

Form 3. It was difficult to obtain crystals of this form at will, and preparations were often contaminated by crystals of form 1 or 2. This form was usually produced under conditions of high supersaturation.

The preparation which first yielded crystals of form 3 was made as follows. Acetylacetone (0·36 ml., B.D.H., not further purified) was added to aqueous uranyl nitrate (5 ml., containing 0·89 g. of the hexahydrate) and the mixture heated nearly to the b. p. Sodium hydroxide solution (0·9 ml., 3·21N) was added dropwise, the last few drops giving a slight precipitate (probably of $UO_3,2H_2O$). The solution was allowed to cool: when the temperature reached 47° crystallisation occurred very rapidly, giving small red needles, yield 0·39 g. (Found: U, 49·2, 48·6%).

It was prepared on a larger scale by adding sodium hydroxide solution (16 ml., 3·0N) to uranyl nitrate hexahydrate (20·0 g.) and acetylacetone (8 ml. of the purified product) in water (60 ml.) at 65°, and seeding with crystals from the first preparation. The product (form 3, contaminated by a very few crystals of form 1) was filtered off and dried in air, yield 8·1 g. (Found: U, 48·25, 48·26, 48·32, 48·28%). After drying over KOH for 1¼ hours at 20°/10 mm. the analysis was substantially unchanged (Found: U, 48·31, 48·11, 48·30). A portion was dehydrated (P_2O_5) for 3½ hr. at 100°/0·02 mm. and gave a fine orange powder resembling that from forms 1 and 2 (Found: U, 50·99, 50·89, 50·99%).

Thorium acetylacetone was prepared by mixing aqueous solutions of thorium nitrate and sodium acetylacetone, and extracting the precipitate with hot toluene. The toluene solution crystallised on standing and the product was recrystallised from warm toluene, m. p. 170·5° (Marchi [27] reported m. p. 171°).

Crystallography.—Densities were determined by flotation in mixtures of tetrabromoethane and tetralin, pre-saturated with uranyl acetylacetone.

Copper K_α radiation ($\lambda = 1·542$ Å) was used. The following diffraction photographs were obtained:

Form 1A. Oscillation photographs, and zero to third layer equi-inclination Weissenberg photographs about the *b* axis.

Form 1B. Oscillation photographs about the *a*, *b*, and c^* axes; equi-inclination Weissenberg photographs of the zero to fourth layers about the *a* axis, and of the zero to third layers about the *b* axis.

Form 2. Oscillation photographs, and zero to second layer equi-inclination Weissenberg photographs about both *a* and *b* axes.

Form 3. Oscillation photographs, and zero to second layer equi-inclination Weissenberg photographs about the *c* axis.

X-Ray powder photographs of forms 1 and 2, and of the transformation products of forms 1 and 3, were taken with a Guinier-type focusing camera.

Infrared Spectra.—Samples were examined as Nujol mulls between sodium chloride plates. The spectra from 700 to 3000 cm.$^{-1}$ were obtained in a Grubb-Parsons double-beam infrared spectrophotometer with an S3A monochromator and a sodium chloride prism. The spectra from 3000 to 3800 cm.$^{-1}$ were obtained on a Hilger double-beam infrared spectrophotometer, model H 800, with a lithium fluoride prism.

Visible and Ultraviolet Absorption Spectra.—The Harwell recording spectrophotometer was used to obtain the solution spectra. The crystal spectra were measured by Dr. G. T. Rogers on a Unicam spectrophotometer, model SP.500, in conjunction with a cell previously described.[28] The crystal of form 1 was 0·21 mm. thick, with approximately parallel faces, and completely covered the hole (1 mm. diam.) in the metal block on which it was mounted. No single crystal of form 3 was available which would completely cover this hole, so seven long crystals, ranging in thickness from 0·15 to 0·20 mm., were laid side by side over the hole and glued in position.

Conductance Measurements.—Measurements were made at 1000 c.p.s. with a bridge similar to that described by Luder.[29] Tests, in which the cell was replaced by a standard resistance box in parallel with a variable air capacitor, showed that the bridge was accurate to ±0·2%.

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[27] Marchi, Ph.D. Thesis, Ohio, 1942, p. 40.
[28] Mclaren and Rogers, *Proc. Roy. Soc.*, 1957, *A*, **240**, 484.
[29] Luder, *J. Amer. Chem. Soc.*, 1940, **62**, 89.

The cell was made of " Pyrex " glass in the form of a cylinder 9 cm. high by 4 cm. diam., with a restricted opening at the top and the electrodes set vertically in the base. The electrodes were of bright platinum, about 2·5 cm. square and 3 mm. apart. A tube which joined the base of the cell served to admit a stream of argon to expel carbon dioxide. The cell-constant was measured by comparison with a cell of larger cell-constant, which had been calibrated by 0·01D-potassium chloride solution; the value at 25° was 0·0358 $cm.^{-1}$ and its variation with temperature was neglected.

The 25° thermostat was a stirred bath of " liquid paraffin," regulated to better than $\pm 0·05°$ by a variable-contact mercury thermometer. The thermostat used for the low-temperature work was a metal can of stirred kerosene standing in a stirred bath of ice and water: the temperature of the kerosene remained at $0·2 \pm 0·1°$ for several hours after filling the ice-bath.

The water was purified by distilling " AnalaR " redistilled water, slightly acidified by potassium hydrogen sulphate, in a simple " Pyrex " still, and collecting it in a silica flask. Soon after preparation, and after removal of carbon dioxide, it had a specific conductance of about $1·2 \times 10^{-7}$ ohm^{-1} at 25°, or 3×10^{-8} ohm^{-1} at 0·2°.

Procedure. A standard quantity (44·6 g.) of water was weighed into the cell and a rapid stream of argon, pre-saturated with water at the same temperature as the cell, was bubbled through it. The stream was interrupted momentarily as each measurement was made. After about 30 min. the conductivity remained constant: on prolonged bubbling of argon the conductivity slowly rose, presumably owing to the solution of ions from the glass or impurities from the argon. When the conductivity had become constant a weighed quantity of uranyl acetylacetone hydrate (form 1, finely ground) was added and measurements were made every minute.

For the experiments at 0·2° the cell was transferred to the cold thermostat after most of the carbon dioxide had been removed from the water, and argon was bubbled again until the conductivity was constant.

In the experiments at 25° the conductivity maxima were observed as the last particles of solid were dissolving. In the experiments at 0·2° the change of slope of the curve occurred also at about this time, but solution was much slower at 0·2° than at 25°.

Identification of the hydrolysis product. Saturated aqueous uranyl acetylacetone was allowed to stand for 2 days in air at room temperature. The fine yellow precipitate was washed once by decantation and then filtered off and allowed to dry in the air. *X*-Ray powder photographs, taken with a Guinier-type focusing camera, were identical with those of $UO_3,2H_2O$ samples.[30]

Solvates.—Crystallisation of uranyl acetylacetone from ethanol. Uranyl acetylacetone monohydrate, form 1 (2·66 g.), was dissolved in warm ethanol (2 ml.) and the solution filtered. The filtrate deposited crystals of the *uranyl acetylacetone–ethanol* adduct at room temperature, and the yield was improved (to 1·48 g.) by cooling to 0° [Found: U, 46·0, 45·9. $UO_2(C_5H_7O_2)_2,C_2H_5{\cdot}OH$ requires U, 46·3%].

Crystallisation of uranyl acetylacetonate from acetylacetone. Uranyl acetylacetone monohydrate, form 1 (5·0 g.), was crystallised from warm acetylacetone (15 ml.). The resulting *uranyl acetylacetone–acetylacetone* adduct (4·8 g.) consisted of small, orange, 6-sided, twinned plates [Found: U, 41·7, 41·6, 41·6. $UO_2(C_5H_7O_2)_2,C_5H_8O_2$ requires U, 41·9%].

Reaction of uranyl acetylacetone with perchloric acid. Aqueous perchloric acid (1·87N) was added dropwise to uranyl acetylacetone monohydrate, form 1 (5·0 g.), and the mixture stirred continuously. When 5 ml. of acid had been added some of the crystals had dissolved, but the remainder were almost unchanged. Addition of a further 0·6 ml. of acid caused these crystals to dissolve rapidly, crystals of a new compound being simultaneously deposited. These new crystals were filtered off and dried (NaOH), yield 2·5 g. Their microscopical appearance was identical with that of the uranyl acetylacetone–acetylacetone adduct (Found: U, 41·7, 41·2%).

Crystallisation of uranyl acetylacetone from acetophenone. Uranyl acetylacetone monohydrate, form 1 (5·0 g.), was dissolved in warm acetophenone (20 ml.). Slow cooling produced large orange crystals (4·0 g.) of the *uranyl acetylacetone–acetophenone* adduct [Found: U, 40·3, 40·2. $UO_2(C_5H_7O_2)_2,C_8H_8O$ requires U, 40·5%].

Crystallisation of uranyl acetylacetone from dioxan. Uranyl acetylacetone monohydrate, form 1 (4·0 g.), was dissolved in boiling dioxan (20 ml.) and the hot solution filtered from a small amount of yellow solid (probably a UO_3 hydrate). The *uranyl acetylacetone–dioxan* adduct

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[30] Dawson, Wait, Alcock, and Chilton, *J.*, 1956, 3531.

(1·5 g.) crystallised on cooling [Found: U, 42·4, 42·2, 42·4, 42·2. $UO_2(C_5H_7O_2)_2,C_4H_8O_2$ requires U, 42·8%].

Ebullioscopic Measurements.—These were made by Dr. D. C. Bradley, using his technique.[31] Over the concentration range 0·0216—0·3541 g. of uranyl acetylacetone to 15·95 g. of benzene the b. p. rose linearly, with a slope of 0·200° per g. {Found: *M*, 913. Calc. for $[UO_2(C_5H_7O_2)_2]_2$: *M*, 937}.

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[31] Bradley, Gaze, and Wardlaw, *J.*, 1955, 3977.