

*Investigations on the Co-ordinative Power of Uranyl. Part I. The Preparation and Properties of Uranyl Complexes of Certain  $\beta$ -Diketones.*

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Uranyl acetate and nitrate, with some  $\beta$ -diketones, yield a series of complexes of different composition. The constitution of the complexes, their solubilities, and their behaviour toward different reagents show that uranium(vi), bound to six oxygen atoms, is co-ordinatively unsaturated. The properties of some water-insoluble and undissociated nitrato-complexes afford conclusive evidence of the existence of covalent bonds between uranyl and nitrate ions. A polymer complex of benzoylnicotinoilmethane is believed to be an instance of 8-co-ordination around uranium(vi).

DURING recent work on uranyl compounds knowledge has accumulated on the singular properties of uranyl nitrate (cf. Glueckauf and McKay, *Nature*, 1950, **165**, 594; Irving, *Quart. Reviews*, 1951, **5**, 208). This compound is easily soluble in organic solvents containing oxygen atoms capable of electron donation (Guempell, *Bull. Soc. chim. Belg.*, 1929, **38**, 443; Misciatelli, *Gazzetta*, 1930, **60**, 839) and its partition coefficient between water and ethyl ether is very high (Katzin and Sullivan, *J. Phys. Coll. Chem.*, 1951, **55**, 346). Uranyl nitrate, dissolved in such organic solvents, forms a series of hydrates, being associated, on an average, with four water molecules (Katzin and Sullivan, *loc. cit.*; McKay and Mathieson, *Trans. Faraday Soc.*, 1951, **47**, 428; Glueckauf, McKay, and Mathieson, *ibid.*, p. 437; Gardner, McKay, and Warren, *ibid.*, 1952, **48**, 997; Katzin, Simon, and Ferraro, *J. Amer. Chem. Soc.*, 1952, **74**, 1191). Solid compounds which are most often of the formula  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{S}$ ,  $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot \text{S}$ , where S is a solvent organic molecule, have been isolated (Mathieson, *J.*, 1949, S294; Katzin and Sullivan, *loc. cit.*). Evidence of the existence of the ion  $[\text{UO}_2(\text{NO}_3)_3]^-$  (Kaplan, Hildebrandt, and Ader, ANL, 1950, 4520, 4521; Jander and Wendt, *Z. anorg. Chem.*, 1949, **258**, 1) and the features of the spectrum of  $[\text{UO}_2(\text{NO}_3)_3]^+$  (Betts and Michels, *J.*, 1949, S286) have suggested formation of covalent, rather than ionic, bonds between uranyl and nitrate ions (cf. Glueckauf and McKay, *loc. cit.*; Irving, *loc. cit.*).

On the basis of these experimental data which have led to the assumption of an 8-co-ordination involving ten electron orbitals in the complex  $[\text{UO}_2(\text{H}_2\text{O})_4(\text{NO}_3)_2]$ , Glueckauf and McKay (*loc. cit.*) have advanced the hypothesis that uranyl nitrate forms covalent complexes possibly involving 5f-orbitals.

Although Katzin (*Nature*, 1950, **166**, 605) denies that covalent bonds can exist between uranyl and nitrate groups, and therefore deems such an assumption unnecessary, Seaborg and Street (*J. Amer. Chem. Soc.*, 1950, **72**, 2790), Seaborg, Street, and Diamond (quoted in "Comprehensive Inorganic Chemistry," The Actinide Series, Seaborg, Van Nostrand

Company, Inc., New York, 1953, p. 168), and Connick and Hugus (*J. Amer. Chem. Soc.*, 1952, **74**, 6012) favour the suggestion of possible *f*-shell covalency.

To obtain information on this matter, we have investigated the complexing behaviour and co-ordinative power of the uranyl ion, and have studied the behaviour of uranyl acetate and nitrate with certain  $\beta$ -diketones, and the properties of the compounds so obtained.

Some complexes of uranyl and  $\beta$ -diketones have been described, namely, those with acetylacetone (Biltz, *Z. anorg. Chem.*, 1904, **40**, 221), and with ammonia, acetylacetone, and pyridine (Hager, *ibid.*, 1927, **162**, 85). We have considered the following  $\beta$ -diketones (generalised as "diketH"): benzoylacetone (benzacH), dibenzoylmethane (dimetH), picolinoylacetone (picacH), benzoylpicolinoylmethane (picmetH), nicotinoylacetone (nicacH), benzoylnicotinoylmethane (nicmetH), benzoylfuroylmethane (furmethH), 5-acetoacetyl-3-methylisooxazole (isoxacH), 5-benzoylacetyl-3-methylisooxazole (isoxmetH).

In aqueous alcohol, uranyl acetate, with all the above  $\beta$ -diketones except benzoylnicotinoylmethane, forms a series of complexes which crystallise with water and are more or less intensely orange. Their general formula corresponds to  $\text{UO}_2(\text{diket})_2 \cdot n\text{H}_2\text{O}$ , where  $n$  varies from 1 to 2.8. The water is strongly bound and is eliminated only with difficulty over phosphoric oxide at 95–100° under 0.01 mm., the colour of the compounds then becoming generally red or brownish-red. On the other hand, benzoylnicotinoylmethane, with uranyl acetate, forms an anhydrous compound of approximate constitution  $\text{UO}_2(\text{nicmet})_2$  having very different properties (see p. 2370). By mixing aqueous solutions of uranyl nitrate with alcoholic solutions of benzoylpicolinoylmethane and benzoylnicotinoylmethane, compounds of the formulæ  $\text{UO}_2(\text{picmetH})_2(\text{NO}_3)_2$  and  $\text{UO}_2(\text{nicmetH})_2(\text{NO}_3)_2$ , respectively, are formed. The picolinoyl compound can be obtained also by treating the complex  $\text{UO}_2(\text{picmet})_2 \cdot 2.5\text{H}_2\text{O}$  with nitric acid in aqueous alcohol. Both these nitrates, which are orange, behave as true complexes.

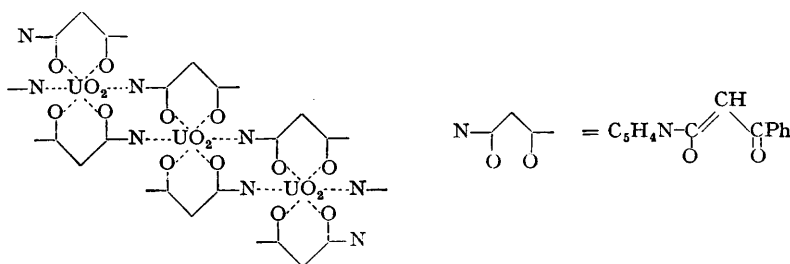
The anhydrous complexes, *e.g.*, of benzoylacetone and dibenzoylmethane, when dissolved or suspended in anhydrous ether, combine with the ether, giving crystalline, yellowish-orange compounds. By addition of anhydrous ammonia or pyridine, compounds of the formulæ  $\text{UO}_2(\text{benzac})_2 \cdot \text{NH}_3$ ,  $\text{UO}_2(\text{benzac})_2 \cdot \text{C}_5\text{H}_5\text{N}$ ,  $\text{UO}_2(\text{dimet})_2 \cdot \text{NH}_3$ , and  $\text{UO}_2(\text{dimet})_2 \cdot \text{C}_5\text{H}_5\text{N}$  are formed.

The complexes of the type  $\text{UO}_2(\text{diket})_2 \cdot n\text{H}_2\text{O}$  are soluble only (or almost solely) in organic solvents containing oxygen atoms capable of electron donation, namely, methyl and ethyl alcohol, acetone, ethyl ether (especially if the last is water-saturated). They are sparingly soluble or insoluble in carbon tetrachloride and carbon disulphide. This behaviour leads to the assumption, which agrees with Martell and Calvin's general views (*cf.* "Chemistry of the Metal Chelate Compounds," Prentice-Hall Inc., New York, 1952, p. 243), that interaction between solvent and solute occurs by direct co-ordination of the solvent molecules to the central metal atom, rather than by polar interaction or hydrogen bonding between solvent molecules and the attached groups. This fact indicates a co-ordinative unsaturation of the uranium central atom; and, since in the uranyl-diketone complexes uranium(vi) is co-ordinatively bound to six oxygen atoms, we must conclude that in these compounds uranium(vi) shows a co-ordination number greater than 6. This view is supported by the behaviour of some uranium(iv) complexes of  $\beta$ -diketones of the formula  $\text{U}(\text{diket})_4$  described by Sacconi (*R. Accad. Lincei*, 1949, [8], **6**, 639), which show solubility properties opposite to those of uranyl diketone complexes. They are, in fact, extremely soluble in carbon tetrachloride, carbon disulphide, and benzene, very sparingly soluble in alcohol and ether. As in these complexes uranium(iv), according to magnetic measurements, is 8-covalent (Sacconi, *loc. cit.*; *cf.* Martell and Calvin, *op. cit.*, pp. 240, 243, 248, 325, 463, etc.) and therefore co-ordinatively saturated, the absence of interactions between the U(iv)-diketone complexes and the molecules of the oxygen-containing solvent supports the conclusion that the solvent molecules containing donor atoms are bound to the uranyl complexes by direct co-ordination to the U(vi) central atom.

The compounds  $\text{UO}_2(\text{picmetH})_2(\text{NO}_3)_2$  and  $\text{UO}_2(\text{nicmetH})_2(\text{NO}_3)_2$  also show a marked tendency to solvation and hydration: indeed, they are soluble only in solvents such as alcohol, acetone, and water-saturated ethyl ether. Evidently, as assumed for uranyl

nitrate (Glueckauf, McKay, and Mathieson, *loc. cit.*; Glueckauf and McKay, *Nature*, *loc. cit.*), the uranium central atom co-ordinates by preference to water which forms, in this way, a "primary" solvation shell, to which the solvent molecules adhere through oxygen-hydrogen bonds (cf. Bockris, *Quart. Reviews*, 1949, **3**, 174). Because of their properties both these complexes can be classified as non-electrolytes: indeed, their electrical conductivity in aqueous ethyl ether is negligible, like that of the inner complexes  $\text{UO}_2(\text{dimet})_2 \cdot 2.5\text{H}_2\text{O}$ , etc. This behaviour affords decisive evidence of the existence of covalent bonds between uranium(vi) and nitrate ions. Both the above-mentioned compounds can be considered as complex entities,  $[\text{UO}_2(\text{picmetH})_2(\text{NO}_3)_2]$  and  $[\text{UO}_2(\text{nicmetH})_2(\text{NO}_3)_2]$ , respectively.

The constitution and properties of the compound corresponding to the formula  $\text{UO}_2(\text{nicmet})_2$  strongly support the conclusion that, in this complex, uranium(vi) shows a co-ordination number greater than 6. Indeed, in agreement with previous studies (Jensen, *Z. anorg. Chem.*, 1944, **252**, 227; Hieber and Brück, *ibid.*, 1952, **269**, 14; Sacconi, *ibid.*, 1953, **271**, 176), the insolubility of this compound in inert organic solvents, its amorphous appearance, and its high thermal stability (at 350° it neither melts nor decomposes) can be interpreted as related to a polymer polynuclear structure of the type shown below.



A structure of such a type implies the 8-co-ordination of the uranium(vi). Moreover, it explains the absence of water in the compound as well as its insolubility in all undissociating solvents. Indeed, it is conceivable that the central uranium atom, being co-ordinatively saturated, will have no capacity to attract molecules of water or oxygenated solvents. Moreover, the solvents such as carbon tetrachloride, carbon disulphide, etc., though they are capable of strong interactions with the groups attached to the uranium, are not able to dissolve the compound on account of its polymeric nature. It can be dissolved only by pyridine, probably through a breaking of the polymer chain and subsequent co-ordination of the pyridinic nitrogen atom to the uranium central atom. The formation of polymer polynuclear complexes including intermolecular co-ordinative bonds from the nitrogen atoms of the nicotinoyl groups has been already demonstrated in the case of some nickel hydrazide complexes (Sacconi, *Gazzetta*, 1953, **83**, 894; *Z. anorg. Chem.*, 1954, **275**, 249). No hypothesis can be advanced about the structure of the 8-co-ordinate bonds in the polynuclear complex. One should remember, however, the arrangement of six coplanar links around the uranium(vi) revealed in the double nitrate  $\text{Rb}[\text{UO}_2(\text{NO}_3)_3]$  (Hoard and Stroupe, quoted in "Spectroscopic Properties of Uranium Compounds," by Dieke and Duncan, McGraw-Hill, New York, 1949, p. 15; cf. Glueckauf and McKay, *loc. cit.*).

#### EXPERIMENTAL

Known  $\beta$ -diketones were prepared according to recorded methods (see Sacconi, *R. Accad. Lincei*, *loc. cit.*). Picolinoylacetone was mentioned by Van Uitert, Fernelius, and Douglas (*J. Amer. Chem. Soc.*, 1953, **75**, 458), but its preparation has not been described.

**Picolinoylacetone.**—Sodium (2.3 g.) was added to a mixture of ethyl picolinate (15 g.), dried acetone (5.8 g.), and anhydrous ethyl ether (50 c.c.) during 20 min. under reflux. The reaction was controlled initially by cooling in ice. After 3 hr., the mixture was warmed at ca. 40° for 30 min. The ochre-yellowish sodium salt of the  $\beta$ -diketone was collected, washed with anhydrous ether, dried, and then added in portions to dilute ice-cooled acetic acid (60 c.c.).

Crystallisation from ethanol-water (charcoal) yielded picolinoylacetone as ivory crystals, m. p. 48—50° (yield 40%) (Found : N, 8.56. Calc. for  $C_8H_9O_2N$  : N, 8.59%).

*Benzoylpicolinoylmethane*.—After addition of sodium (2.3 g.) to ethyl picolinate (15 g.) and acetophenone (12 g.) in anhydrous ether (100 c.c.), subsequent treatment analogous to that above yielded *benzoylpicolinoylmethane* as ivory crystals (50%), m. p. 87—88° (Found : N, 6.26.  $C_{14}H_{11}O_3N$  requires N, 6.22%).

Hydrated uranyl-diketone complexes were obtained by mixing an aqueous solution of uranyl acetate dihydrate (1 mol.) with an alcoholic solution of the  $\beta$ -diketone (2 mol.). Immediately, or after short heating on the steam-bath, crystalline products were precipitated and were recrystallized from alcohol. Samples for analysis were dried ( $H_2SO_4$  in vac.) to constant weight. The compounds were analyzed by conversion into  $U_3O_8$  and weighing. The water content was obtained by dehydration at 100°/0.01 mm. over phosphoric oxide to constant weight.

In the Table, Nos. 1—8 give the results obtained for such compounds, and Nos. 9—15 those for the seven complexes whose preparations are reported below.

(9) *Uranyl-benzoylacetone complex-ammonia*. Dry ammonia is passed through a suspension of the complex 1 (0.7 g.) in anhydrous ether (50 c.c.). Dissolution soon takes place and a yellow precipitate of tabular crystals is formed.

(10) *Uranyl-benzoylacetone complex-pyridine* (A different method of preparing this compound is reported by Hager, *loc. cit.*). Pyridine (4 c.c.) is added to a solution of the complex 1 (1.5 g.) in methyl alcohol (100 c.c.), and the mixture heated on the steam-bath for 1 hr., giving an orange precipitate.

No.	Uranyl complexes	Behaviour on heating	Analysis									
			Found, %					Required, %				
			C	H	N	U	H <sub>2</sub> O	C	H	N	U	H <sub>2</sub> O
1	$UO_2(\text{benzac})_2 \cdot 2.5H_2O$	A	37.45	3.72	—	37.35	—	37.68	3.63	—	37.34	—
2	$UO_2(\text{picac})_2 \cdot 1H_2O$	B	—	—	4.51	38.78	—	—	—	4.57	38.87	—
3	$UO_2(\text{nicac})_2 \cdot 2H_2O$	C	—	—	4.76	37.95	5.70	—	—	4.45	37.79	5.68
4	$UO_2(\text{isoxac})_2 \cdot 2.5H_2O$	D	—	—	4.23	36.74	—	—	—	4.33	36.74	—
5	$UO_2(\text{dimet})_2 \cdot 2.5H_2O$	E	47.78	3.41	—	31.20	5.90	47.31	3.57	—	31.26	5.91
6	$UO_2(\text{picmet})_2 \cdot 2.5H_2O$	F	—	—	3.88	31.04	—	—	—	3.67	31.18	—
7	$UO_2(\text{furmet})_2 \cdot 2.2H_2O$	G	42.57	3.15	—	32.31	—	42.42	3.07	—	32.34	—
8	$UO_2(\text{isoxmet})_2 \cdot 2.8H_2O$	H	—	—	3.59	30.63	—	—	—	3.60	30.65	—
9	$UO_2(\text{benzac})_2 \cdot NH_3$	I	—	—	2.32	39.67	—	—	—	2.30	39.06	—
10	$UO_2(\text{benzac})_2 \cdot C_5H_5N$	J	—	—	2.13	35.35	—	—	—	2.08	35.45	—
11	$UO_2(\text{dimet})_2 \cdot NH_3$	K	—	—	1.89	32.63	—	—	—	1.91	32.45	—
12	$UO_2(\text{dimet})_2 \cdot C_5H_5N$	L	—	—	1.86	30.09	—	—	—	1.76	29.92	—
13	$UO_2(\text{picmetH})_2(NO_3)_2$	M	39.79	2.56	6.66	28.06	—	39.82	2.62	6.63	28.19	—
14	$UO_2(\text{nicmetH})_2(NO_3)_2$	N	39.95	2.64	6.70	28.73	—	39.82	2.62	6.63	28.19	—
15	$[UO_2(\text{nicmet})_2]_2$	O	—	—	3.92	33.40	—	—	—	3.90	33.15	—

A, Above 120° turns red; at 258—259° melts. B, Decomp. at 182—183°. C, Does not melt at 270°. D, Decomposes at 190—205°. E, Above 140° turns red; melts at 267—271° (decomp.). F, Above 215° decomp. G, Above 150° decomp. H, Neither melts nor decomposes at 280°. I, Above 120° darkens to red; melts at 162—164° (decomp.). J, Melts at 242—243° (decomp.). K, Above 140° darkens to red; decomp. at 215°. L, Melts between 235° and 245° (decomp.). M, Decomp. above 170°. N, Decomp. at 210°. O, Neither melts nor decomposes at 350°.

(11) *Uranyl-dibenzoylmethane complex-ammonia*. Dry ammonia is bubbled through a solution of the complex 5 (1.2 g.) in anhydrous ether (100 c.c.). A crystalline precipitate is formed.

(12) *Uranyl-dibenzoylmethane complex-pyridine*. Dry pyridine (4 c.c.) is added to a solution of the complex 5 (1.5 g.) in anhydrous ether (100 c.c.). A crystalline precipitate is suddenly formed.

(13) *Nitrate of uranyl-benzoylnicotinoylmethane complex*. A solution of uranyl nitrate hexahydrate (1 g.) in water (7 c.c.) is mixed with a solution of benzoylnicotinoylmethane (1.1 g.) in alcohol (20 c.c.). The intensely orange precipitate is recrystallized from alcohol.

(14) *Nitrate of uranyl-benzoylpicolinoylmethane complex*. A solution of uranyl acetate dihydrate (1 g.) in water (10 c.c.) is mixed with a solution of benzoylpicolinoylmethane (1 g.) in alcohol (40 c.c.). The precipitate so formed is dissolved by heat and addition of a few c.c. of concentrated nitric acid and alcohol (50 c.c.). On cooling, an orange crystalline precipitate is formed. It can also be prepared as for No. 13.

(15) *Uranyl-benzoylnicotinoylmethane complex*. A solution of uranyl acetate (1 g.) in water

(10 c.c.) is mixed with a solution of benzoynicotinoylmethane (1 g.) in alcohol (50 c.c.). After short heating on the steam-bath, the amorphous yellowish-orange precipitate formed is filtered off. It is insoluble in water and in all inert organic solvents, but sparingly soluble in pyridine.

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