

*Investigation on the Co-ordinative Power of Uranyl. Part II.**
Absorption Spectra of the Complexes with β -Diketones.

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Absorption spectra of anhydrous and aqueous organic solutions of uranyl complexes afford experimental evidence of the existence of strong bonds (essentially covalent) between the uranium central atom and the ligands, and show that the complexes are solvated and hydrated to a high degree. This supports the conclusion that in such complexes uranium(vi) exhibits a co-ordination number greater than 6.

THE study of the spectra of uranyl compounds has thrown light on their constitution and on the character of bonds, the interaction with solvents, etc. (cf. Dieke and Duncan, "Spectroscopic Properties of Uranium Compounds," McGraw Hill, New York, 1949; Kiss and Nyiri, *Z. anorg. Chem.*, 1942, **249**, 340), and we have therefore carried out spectrophotometric measurements on solutions of these compounds and various β -diketones in order to obtain information on the complexes so formed.

EXPERIMENTAL

Visible and ultra-violet absorption spectra of solutions of the complexes referred in Part I* were measured with a Beckman DU quartz spectrophotometer and silica cells 0.999 cm. long.

Methyl and ethyl alcohols and ethyl ether used as solvents were carefully purified (cf. Harrison, Lord, and Loofbourow, "Practical Spectroscopy," Prentice-Hall, New York, 1948, p. 418). Aqueous solvents were: 98% methyl and ethyl alcohols, and diethyl ether (saturated with water at 20—22°). The solutions were 16.9×10^{-2} mm with respect to β -diketones and half this concentration (*i.e.*, equivalent) with respect to uranyl complexes.

TABLE 1.

Compound	Solvent *	λ (m μ)	$\log \epsilon$	λ (m μ)	$\log \epsilon$	Compound	Solvent *	λ (m μ)	$\log \epsilon$	λ (m μ)	$\log \epsilon$
Picolinoylacetone	A, B	225	3.77	313	4.13	Benzoylpicolinoyl-	A, B, C,	245	3.91	341	4.31
Nicotinoylacetone	A, B, C	236	3.80	307	4.14	methane	D, E, F	245	3.90	341	4.31
		236	3.79	307	4.13			245	3.92	341	4.35
		236	3.80	307	4.13			245	3.92	341	4.36
5-Acetoacetyl-3-	A, B, D	249	3.71	310	4.10			237	3.91	342	4.29
methyliso-		249	3.72	310	4.11			237	3.90	342	4.28
oxazole		249	3.74	310	4.13	Benzoylnicotinoyl-	A, B, C	246	3.90	339	4.27
5-Benzoylacetyl-3-	A, B, D,	256	3.85	340	4.25	methane		246	3.89	339	4.27
methyliso-	E	256	3.85	340	4.25			246	3.91	339	4.27
oxazole		256	3.86	340	4.25						

* A = Anhydrous EtOH; B = 98% EtOH; C = anhydrous MeOH; D = aqueous Et₂O; E = anhydrous Et₂O; F = 98% MeOH.

In Table 1 are given spectral positions (in m μ) and intensities (in $\log \epsilon/M$) of characteristic maxima for the β -diketones. Experimental absorption curves for β -diketones and complexes are shown in the Figures and recorded in Table 2, where *D* signifies optical density. β -Diketones dissolved in different solvents give almost identical curves, so only one curve is given for each.

* Part I *J.*, 1954, 2368.

TABLE 2.

Reagents and complexes *	Solvent †	$\lambda_{\max.}$		$\lambda_{\min.}$		$\lambda_{\max.}$		$\lambda_{\min.}$		$\lambda_{\max.}$		$\lambda_{\min.}$	
		$\lambda_{\max.}$	D	$\lambda_{\min.}$	D	$\lambda_{\max.}$	D	$\lambda_{\min.}$	D	$\lambda_{\max.}$	D	$\lambda_{\max.}$	D
Benzoylacetone	A, B	248	0.96	263	0.61	309	2.34	—	—	—	—	—	—
UO ₂ (benzac) ₂	A	263	1.65	280	1.54	305	1.66	355	0.61	377	0.69	—	—
"	B	250	1.37	260	1.27	308	2.11	360	0.35	378	0.38	—	—
Benzoylacetone	D, E	248	1.00	264	0.67	309	2.42	—	—	—	—	—	—
UO ₂ (benzac) ₂	E	258	1.82	290	1.48	303	1.53	355	0.61	378	0.83	—	—
"	D	251	1.49	262	1.34	307	2.16	355	0.46	378	0.59	—	—
Benzoylacetone	C, F	248	0.98	265	0.60	309	2.20	—	—	—	—	—	—
UO ₂ (benzac) ₂	C	255	1.65	280	1.62	307	1.82	355	0.59	376	0.66	—	—
"	F	255	1.62	280	1.60	307	1.80	356	0.58	376	0.64	—	—
Dibenzoylmethane	A, B	253	1.46	275	0.80	342	> 3.0	—	—	—	—	—	—
UO ₂ (dimet) ₂	A	275	2.55	310	1.64	334	2.04	365	1.27	394	1.50	—	—
"	B	257	1.98	300	1.64	340	> 3.0	387	0.83	394	0.84	—	—
Dibenzoylmethane	D, E	253	1.53	275	0.80	340	> 3.0	—	—	—	—	—	—
UO ₂ (dimet) ₂	E	269	2.91	305	1.51	334	2.07	360	1.23	396	1.88	—	—
"	D	261	2.40	300	1.52	334	2.66	380	1.17	396	1.30	—	—
Dibenzoylmethane	C, F	253	1.51	275	0.81	342	> 3.0	—	—	—	—	—	—
UO ₂ (dimet) ₂	C	269	2.45	305	1.66	336	2.16	375	1.33	395	1.45	—	—
"	F	269	2.45	305	1.71	336	2.25	375	1.33	394	1.45	—	—
Picolinoylacetone	A, B	228	1.00	258	0.46	317	2.20	—	—	—	—	—	—
UO ₂ (picac) ₂	A	246	1.69	265	1.07	316	1.48	360	0.76	376	0.80	—	—
"	B	237	1.46	260	1.00	310	1.85	365	0.47	380	0.51	—	—
"	C	243	1.39	265	0.91	314	1.44	360	0.56	376	0.58	—	—
Nicotinoylacetone	A, B	236	1.03	254	0.41	307	2.25	—	—	—	—	—	—
UO ₂ (nicac) ₂	A	250	1.61	283	0.96	323	1.50	—	—	—	—	—	—
"	B	240	1.55	270	1.19	307	1.67	360	0.48	378	0.57	—	—
"	C	247	1.66	280	1.14	308	1.42	355	0.58	376	0.68	—	—
5-Acetoacetyl-3-methyl- isooxazole	A, B	249	0.86	266	0.54	310	2.11	—	—	—	—	—	—
"	D, E	249	0.92	266	0.85	310	2.43	—	—	—	—	—	—
UO ₂ (isoxac) ₂	A	261	1.66	290	1.15	320	1.37	350	0.72	378	0.89	—	—
"	E	266	1.71	290	1.19	306	1.31	314	1.29	320	1.31	—	—
"	D	266	1.66	285	1.32	306	1.55	350	0.62	378	0.96	—	—
Nicotinoylbenzoylmethane	A, B, C	246	1.34	280	0.74	339	3.10	—	—	—	—	—	—
UO ₂ (nicmetH) ₂ (NO ₃) ₂	A, B	253	1.60	220	1.38	335	2.78	385	0.75	399	0.84	—	—
"	C	260	1.87	298	1.58	336	2.60	383	1.04	396	1.13	—	—
5-Benzoylacetyl-3-methyl- isooxazole	A, B	256	1.19	280	0.75	340	2.98	—	—	—	—	—	—
UO ₂ (isoxmet)	A, B	280	2.27	312	1.32	333	1.64	360	1.10	395	1.70	—	—
5-Benzoylacetyl-3-methyl- isooxazole	D, E	256	1.23	280	0.26	340	2.98	—	—	—	—	—	—
UO ₂ (isoxmet) ₂	E	280	2.61	310	1.35	333	1.79	360	1.04	397	1.95	—	—
"	D	277	2.28	308	1.30	333	1.86	363	1.15	397	1.65	—	—

* For abbreviations, see Part I (pp 2369—2370).

† See Table 1.

RESULTS AND DISCUSSION

(1) The spectra obtained for the β -diketones have essentially the same general shape and show two bands, one in the 225—256- $m\mu$ and the other in the 307—349- $m\mu$ region. Values for benzoylacetone and dibenzoylmethane agree with those recorded by Morton *et al.* (*J.*, 1934, 883), according to whom the absorbing entities are complex chromophores. The 225—256- $m\mu$ maximum was ascribed to the phenyl group influenced by the carbonyl group, and that near 307—349 $m\mu$ to the carbonyl group. In terms of modern views, the absorption maximum at 307—349 $m\mu$ should be referred to the enol form of the β -diketones, stabilized through a chelation involving a hydrogen bond. The resulting enol ring is then stabilized through both hydrogen-bond formation and enol resonance (cf. Ferguson, "Electron Structure of Organic Molecules," Prentice-Hall, New York, 1952, pp. 216, 218).

(2) The nature of the solvent (methanol, ethanol, and ethyl ether, anhydrous or aqueous) scarcely affects the spectra of diketones, particularly those of benzoylacetone and dibenzoylmethane. This last fact is probably associated with the absence of polar atoms in the groups attached to the carbonyl carbon atom of both β -diketones, which produces weaker interaction with the molecules of the polar solvents.

(3) The absorption curves obtained for the complexes, except those of benzoylpicolinoylmethane, show three bands, at 240—280, 303—340, and 376—403 $m\mu$, respectively. The first two correspond essentially to those of the complexing agents, but the first is shifted

FIG. 1.

FIG. 2.

FIG. 3.

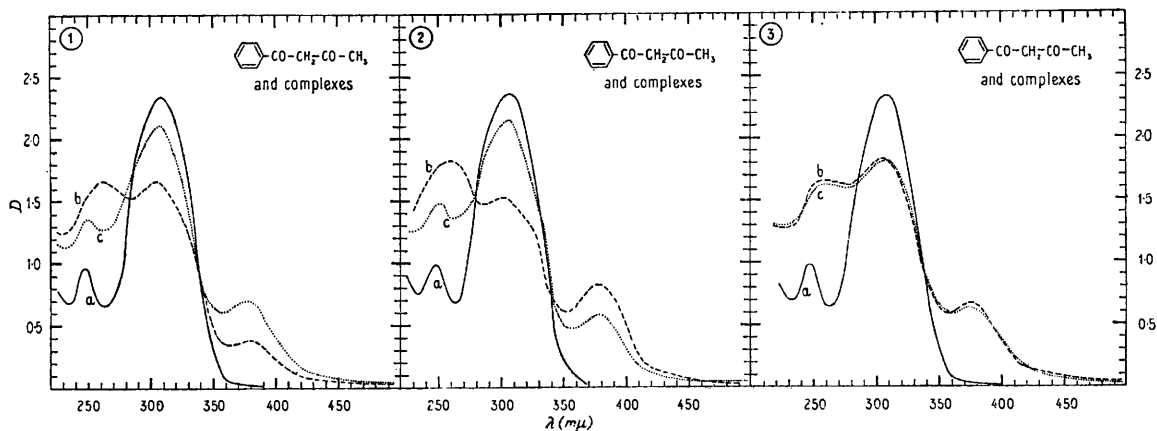


FIG. 1. *a*, Benzoylacetone in anhydrous and 98% EtOH; *b*, $\text{UO}_2(\text{benzac})_2$ in anhydrous EtOH; *c*, $\text{UO}_2(\text{benzac})_2$ in 98% EtOH.

FIG. 2. *a*, Benzoylacetone in anhydrous and aqueous Et_2O ; *b*, $\text{UO}_2(\text{benzac})_2$ in anhydrous Et_2O ; *c*, $\text{UO}_2(\text{benzac})_2$ in aqueous Et_2O .

FIG. 3. *a*, Benzoylacetone in anhydrous and 98% MeOH; *b*, $\text{UO}_2(\text{benzac})_2$ in anhydrous MeOH; *c*, $\text{UO}_2(\text{benzac})_2$ in 98% MeOH.

FIG. 4.

FIG. 5.

FIG. 6.

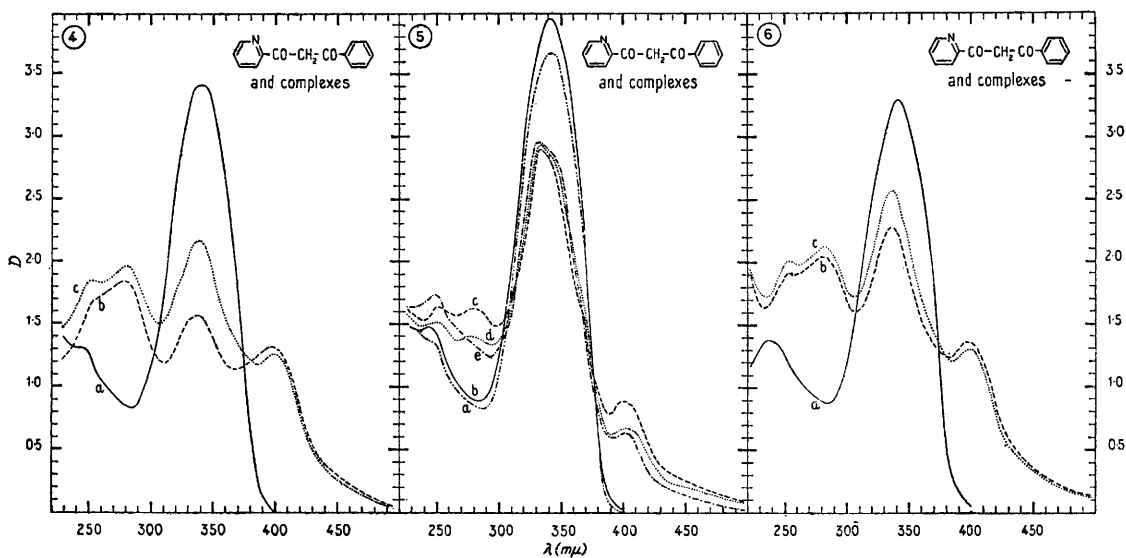


FIG. 4. *a*, Benzoylpicolinoylmethane in anhydrous and 98% EtOH; *b*, $\text{UO}_2(\text{picmet})_2$ in anhydrous EtOH; *c*, $\text{UO}_2(\text{picmet})_2$ in 98% EtOH.

FIG. 5. *a*, Benzoylpicolinoylmethane in anhydrous Et_2O ; *b*, Benzoylpicolinoylmethane in aqueous Et_2O ; *c*, $\text{UO}_2(\text{picmetH})_2(\text{NO}_3)_2$ in anhydrous EtOH; *d*, $\text{UO}_2(\text{picmetH})_2(\text{NO}_3)_2$ in 98% EtOH; *e*, $\text{UO}_2(\text{picmetH})_2(\text{NO}_3)_2$ in aqueous Et_2O .

FIG. 6. *a*, Benzoylpicolinoylmethane in anhydrous and 98% MeOH; *b*, $\text{UO}_2(\text{picmetH})_2(\text{NO}_3)_2$ in anhydrous MeOH; *c*, $\text{UO}_2(\text{picmetH})_2(\text{NO}_3)_2$ in 98% MeOH.

towards longer wave-lengths with a hyperchromic effect; the second is shifted generally towards shorter wave-lengths with a hypochromic effect. The third band is lacking in the spectra of β -diketones.

The spectra of the complexes of benzoylpicolinoylmethane exhibit two inflections instead of the former maximum.

(4) The absorption curves of each complex usually vary slightly with solvent.

(5) A greater variation in spectra is exhibited by each of these complexes according as it is dissolved in an aqueous or an anhydrous solvent. The differences are particularly large for benzoylacetone and dibenzoylmethane complexes, and for ethyl ether as solvent; on the contrary they often are slight or even absent for anhydrous and aqueous-alcoholic solutions.

The absorption curves obtained for the complexes differ largely in shape and features from those of the β -diketones and from those of solutions of uranyl sulphate and nitrate reported by Betts and Michels (*J.*, 1949, S 282) and by Mathieson (*ibid.*, p. S 298). They differ also from the spectrum of aqueous solutions of uranyl perchlorate, in which uranyl exists essentially as an aquo-ion (cf. Sutton, Report 1612, National Research Council, Ottawa, Canada; Betts and Michels, *loc. cit.*, pp. 288, 289; Kiss and Nyiri, *loc. cit.*). The bands of the complexes in the 303—340- $m\mu$ region, where the band of uranyl ion also occurs, show a negative effect, being less intense than those of the β -diketones at 307—349 $m\mu$.

In the spectra of the complexes, instead of the assembly of eleven bands of uranyl with a maximum at *ca.* 416 $m\mu$, there appears a band with the maximum shifted toward shorter wave-lengths, at 376—403 $m\mu$. According to Ferguson (*op. cit.*, p. 46), this decrease in the wave-length of the maximum reflects chelation between the central atom and the ligands. It can be assumed that this new band is produced from some new electron transition which accompanies the interaction of the chelate groups with the uranium central atom. The stability of the complexes should be proportional to this hypsochromic effect.

It should be emphasized that this band shows a continuous shape without structure, quite different from the sharp line-like band envelopes of uranyl in the 360—490- $m\mu$ region. As is well known, the distinct structure of the uranyl spectrum, with sharp bands somewhat like the rare-earth spectra, is ascribed to definite transitions from vibration, rotation, and electronic levels (cf. Brode, "Chemical Spectroscopy," John Wiley & Sons, Inc., New York, 1947, p. 267) owing to incompleteness of the *5f*, *6d*, *7s*, and *7p* shells, which permit electron-level transitions. Indeed, only a part of the 16 orbitals above mentioned, presumably the *7s* and *7p*, are involved in the bonds with the two oxygens of UO_2 (cf. Glueckauf and McKay, *Nature*, 1950, 165, 594). The disappearance of this distinct structure in the uniform bands of the complexes at 376—403 $m\mu$ shows that the possibility of level transitions is diminished owing to diminution in the incompleteness of levels because of electron-donation to the uranium central atom from electron-donor oxygen atoms of the ligands. This affords evidence of the existence of strong co-ordinative bonds, essentially covalent in character, between the uranium central atom and the donor groups, here including the NO_3 groups of the nitrate complexes.

The shifts of the original bands of the free ligand molecules from 225—256 and 307—349 $m\mu$ towards 240—280 and 303—340 $m\mu$ in the spectra of the complexes can be ascribed to the polarization suffered by the ligands in consequence of the co-ordination around the uranium central atom.

The singular features of the spectra of benzoylpicolinoylmethane complexes can be correlated with the presence of the *ortho*-nitrogen atom in the pyridinic ring of the diketone molecule. Since the maximum near 280 $m\mu$ is lacking in the spectra of the ligand, we can assume that such a feature is due to interactions between the nitrogen atom and the uranium central atom.

The change in the absorption curve for each complex, especially for the complexes of benzoylacetone and dibenzoylmethane, from solvent to solvent, and the larger change when an anhydrous solvent is substituted for the aqueous one, reflects the strong interaction between the molecules of the complex and those of the organic solvent or water, which results in solvation.

In the case of the curves of aqueous ethanol and ethyl ether solutions of the complexes of benzoylacetone and dibenzoylmethane, the hypochromic effect on the band near 263 and 270 $m\mu$ and the hyperchromic effect on the maxima at 305 and 336 $m\mu$ are notable. The very remarkable decrease in intensity of the maxima at 378 and 390 $m\mu$, respectively, above ascribed to the chelated uranium(VI), as compared with the intensities of the maxima for the solutions in the same anhydrous solvents, should also be emphasized.

This hypochromic effect, which could be even considered as a "dampening effect" (Brode, *op. cit.*, p. 231) analogous to that observed by Mathieson (*J.*, 1949, S 298) for organic and aqueous solutions of uranyl nitrate, can be ascribed to the formation of hydrates, *i.e.*, to replacement of the bonds between uranium and organic molecules by stronger bonds between uranium and water, a substitution which should cause a lowering of the vibrational properties of the electronic system of uranyl. Thus, these experimental results suggest that, in aqueous-organic solutions of the complexes, water molecules replace the organic "solvation" molecules, with formation of a "primary" hydration shell. This agrees with Glueckauf's views and with those of Katzin *et al.* (*J. Phys. Colloid Chem.*, 1951, 51, 346; *Trans. Faraday Soc.*, 1951, 47, 438; *J. Amer. Chem. Soc.*, 1952, 74, 1191) on solutions of uranyl nitrate in aqueous organic solvents.

As mentioned above, the change in spectra from anhydrous to aqueous solutions is very strong for the complexes of benzoylacetone and dibenzoylmethane. Since these ligands when bound in the complexes have no polar atoms capable of strong interactions with the solvent molecules, the view is supported that the observed interactions occur between water or organic molecules and the uranium central atom, and therefore that they are co-ordinative in nature. Thus the co-ordinative unsaturation of uranium(VI) bound in these complexes is further supported.

This effect is much less evident, or even absent, in the spectra of alcoholic solutions. This fact is analogous to anomalous behaviour of uranyl nitrate-water-alcohol systems, referred by Katzin and Sullivan (*J. Phys. Coll. Chem.*, 1951, 55, 346), Mathieson and McKay (*Trans. Faraday Soc.*, 1951, 47, 428), and Glueckauf, McKay, and Mathieson (*ibid.*, p. 437). According to the assumption of these authors in the case of aqueous-alcoholic solutions of uranyl nitrate, it may be assumed that, for such solutions of uranyl complexes too, a competition exists between the molecules of alcohol and the molecules of water co-ordinated around the uranium central atom, *i.e.*, that alcohol molecules, by virtue of their hydroxyl groups, can replace some water of hydration. In this way, the "primary" solvation shell will not differ greatly from anhydrous to aqueous alcohol solutions. This assumption explains the similarity between several of the spectra of such complexes in anhydrous and in aqueous-alcohol solutions.

The fact that absence of change in spectrum of complexes has been found chiefly for anhydrous and aqueous methyl alcohol solutions, can be fully explained on the basis of steric considerations. Indeed, the small size of the methanol molecules, in contrast to that of ethanol, allows them to penetrate more easily as far as the uranium central atom "screened" by the voluminous donor groups packed around it. In such a way the methanol molecules will be able to compete with the hydrating molecules and displace them.

Conclusions.—From these spectrophotometric investigations we conclude that: (1) The co-ordination bonds between the uranium central atom and the ligands are strong, probably covalent in character. (2) The complexes, in various anhydrous and aqueous solvents, have a high tendency to form solvates and hydrates. (3) The attractions between uranium and water molecules and between uranium and organic molecules are rather strong and should be considered as co-ordinative forces. (4) Uranium(VI) in these complexes has a tendency to manifest a co-ordination number greater than 6.

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