865. *Investigations on the Co-ordinative Power of Uranyl. Part III.* Infrared Spectra of Some Complexes with β-Diketones.*

By L. Sacconi, G. Caroti, and P. Paoletti.

Infrared absorption spectra have been obtained for a number of uranyl complexes with acetylacetone, benzoylacetone, and dibenzoylmethane, crystallised with water, ammonia, or pyridine and in the anhydrous state. Despite the complexity of the spectra the two ν_1 and ν_3 frequencies assigned to the bent form of the uranyl group have been observed for some of such compounds. In the anhydrous complexes of benzoylacetone and dibenzoylmethane such frequencies are shifted and altered in intensity probably owing to the modified crystal field of the " surroundings " of uranyl. The frequencies and the features of the absorption bands of water indicate different types of hydrogen bonding and confirm the existence of co-ordinate bonds between uranium and water molecules in the hydrated complexes. The H–N stretching vibrations of the ammonia appear to be shifted to lower frequencies, a feature regarded as characteristic of nitrogen-to-metal bonds.

A most interesting problem in the chemistry of uranium is that of the stereochemistry of the uranyl group. Although *X*-ray diffraction indicates that the UO_2 radical is

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* Part II, Sacconi and Giannoni, *J.*, 1954, 2751.

linear,[1-3] Raman and infrared spectra even if not unambiguous, appear to favour a bent form.[4-7]

The structure of the uranyl radical is closely related to the co-ordination number and the nature of co-ordinate bonds of which this radical is capable. Data show that in some uranyl compounds, *e.g.*, the nitrate, the uranium atom is octaco-ordinated, and that the central atom forms six bonds which have some degree of covalent character and are in a plane orthogonal to the O–U–O bonds. Thus the uranyl group would show sexa-covalency and therefore involve the use of *f* orbitals.[8] Most of the evidence in favour of this assumption is based on the strong tendency of the uranyl group to co-ordinate molecules of water in the solid state and in solution, as shown by, *e.g.*, solubility, partition, conductometric, and thermochemical measurements.[9]

In Parts I [10] and II * it was found that also in complexes with β-diketones the uranyl group, even when bonded to two diketone radicals, appears to be co-ordinatively unsaturated and tends to co-ordinate donor molecules, *e.g.*, water, alcohols, nitrogen bases, etc. In order to get more information on the stereochemistry of the uranyl group and its co-ordinating power we investigated the infrared spectra of these, and some other complexes.

Experimental.—Preparation of complexes. Those with benzoylacetone and dibenzoylmethane were prepared as described previously.[10] Those with acetylacetone were prepared according to Biltz and Hager.[11]

The monohydrate of the dibenzoylmethane complex, *aquobis(dibenzoylmethane)uranyl*, was prepared as follows: the anhydrous complex was finely ground with hexachloro-1 : 3-butadiene, its colour changing from red-brown to orange-yellow. On evaporation of the solvent in air a yellowish-orange powder was obtained (Found: C, 48·9; H, 3·2; U, 32·4. $C_{30}H_{22}O_6U,H_2O$ requires C, 49·0; H, 3·3; U, 32·4%).

Absorption spectra. The spectra were taken with a Perkin-Elmer 21 recording spectrophotometer fitted with a rock-salt prism, and a 12C spectrophotometer fitted with a lithium fluoride prism. The samples were examined as Nujol mulls and in some cases, in the 3μ region, in mulls of fluorocarbon.

RESULTS AND DISCUSSION.

Absorption of Uranyl.—The vibrations of the UO_2 group are characterised [4] by three frequencies, ν_2, 210 cm.$^{-1}$; ν_1, 860 cm.$^{-1}$; ν_3, 930 cm.$^{-1}$. If the UO_2 group is not linear all three frequencies should be active both in the Raman and in the infrared spectra, but if it is linear only ν_1 should be Raman-active, and ν_2 and ν_3 only infrared-active. Conn and Wu [4] examined the Raman spectrum of uranyl nitrate, chloride, and sulphate and found the frequencies ν_1 and ν_2, while in the infrared spectra of the chloride and the acetate ν_3 and ν_1 were observed; the latter was not always established with certainty because it is weak and overlaps the very intense ν_3 band. The frequency ν_2 is outside the range of observation in the infrared region. These results were interpreted as indicating the non-linearity of the UO_2 group.

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[1] Fankuchen, *Phys. Rev.*, 1933, **43**, 327, 1048; *Z. Krist.*, 1935, **91**, 473; 1936, **94**, 212.

[2] Zachariasen, *Acta Cryst.*, 1948, **1**, 277, 281.

[3] Horton, *J. Amer. Chem. Soc.*, 1956, **78**, 897.

[4] Conn and Wu, *Trans. Faraday Soc.*, 1938, **34**, 1483.

[5] Lecomte and Freymann, *Bull. Soc. chim. France*, 1941, **8**, 622.

[6] Satyanarayana, *Proc. Indian Acad. Sci.*, 1942, *A*, **15**, 414.

[7] Sevcenko and Stepanov, *Zhur. eksp. teoret. Fiz.*, 1949, **19**, 1113.

[8] Glueckauf and McKay, *Nature*, 1950, **165**, 594; Irving, *Quart. Reviews*, 1951, **5**, 208; Street and Seaborg, *J. Amer. Chem. Soc.*, 1950, **72**, 2790; Connick and Hugus, jun., *ibid.*, 1952, **74**, 6012; Coulson and Lester, *J.*, 1956, 3650.

[9] Katzin and Sullivan, *J. Phys. Colloid Chem.*, 1951, **55**, 346; McKay and Mathieson, *Trans. Faraday Soc.*, 1951, **47**, 428; Glueckauf, McKay, and Mathieson, *ibid.*, p. 437; Gardner, McKay, and Warren, *ibid.*, 1952, **48**, 997; Coulter, Pitzer, and Latimer, *J. Amer. Chem. Soc.*, 1940, **62**, 2845; Kapustinskii and Baranova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1952, 1122; McKay, *J. Inorg. Nuclear Chem.*, 1957, **4**, 375.

[10] Sacconi and Giannoni, *J.*, 1954, 2368.

[11] Biltz, *Z. anorg. Chem.*, 1904, **40**, 221; Hager, *ibid.*, 1927, **162**, 1927.

Lecomte and Freymann [5] examined the infrared spectra of about twenty uranyl salts and found always an intense band between 907 and 940 cm.$^{-1}$, and in many of these salts a weak band at about 850 cm.$^{-1}$; they therefore favoured a non-linear UO_2 group. The same conclusion was reached by Satyanarayana [6] from Raman spectroscopy. More recently, Sevcenko and Stepanov [7] examined the infrared spectra of uranyl sulphate, the potassium double sulphate, the nitrate, and the acetate. They did not always find the fundamental vibration at 860 cm.$^{-1}$, possibly owing to limitations in their apparatus, but took into account also the harmonics. They concluded that the uranyl group is probably bent in the sulphate and practically linear in the other two salts.

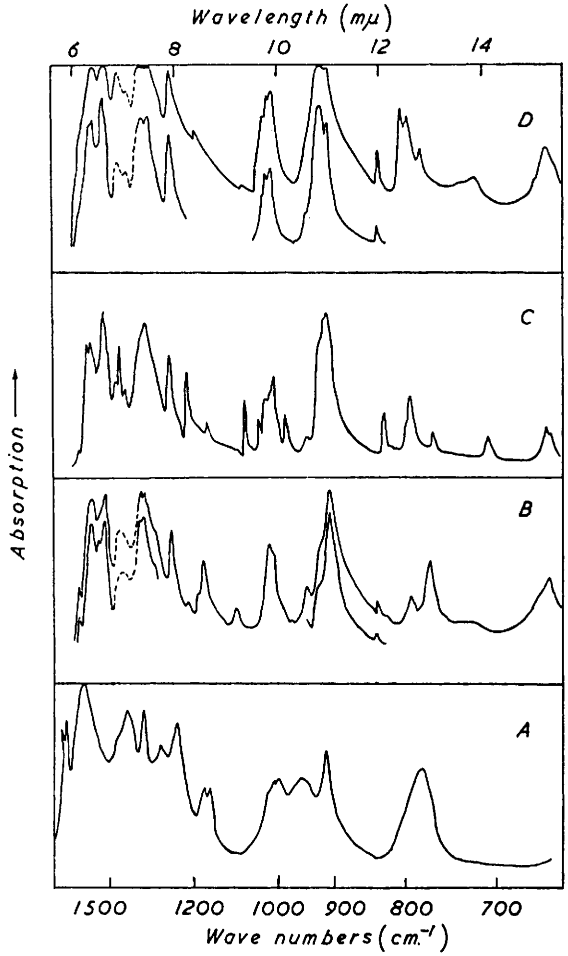

FIG. 1.* *Spectra of acetylacetone and* UO_2 *complexes*:

(*A*) Acetylacetone.
(*B*) $UO_2(acetac)_2,NH_3$.
(*C*) $UO_2(acetac)_2,C_5H_5N$.
(*D*) $UO_2(acetac)_2,H_2O$.

* In these legends, the following abbreviations are used for the diketone residues:

acetac = acetylacetone.
benzac = benzoylacetone.
dimet = dibenzoylmethane.

In short, the conclusions derived from infrared spectroscopy are ambiguous because the two bands attributed to a bent form of the uranyl group have not always been observed with certainty.

To explain the foregoing inconsistencies, Crandall [12] assumes that in solution the " co-ordinating " power of the ions surrounding the uranyl group can change the shape from linear to bent, shifting the vibration of the uncomplexed ion and breaking the selection rules for the gaseous ion. Sutton,[13] on the basis of Raman measurements, confirmed the

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[12] Crandall, *J. Chem. Phys.*, 1949, 17, 602.

hypothesis that in solution the linear uranyl ion is perturbed by strong fields. On the other hand, a re-examination of some old infrared and Raman spectroscopic data in the light of studies of fluorescence spectra, favours a linear structure for the uranyl radical.[14]

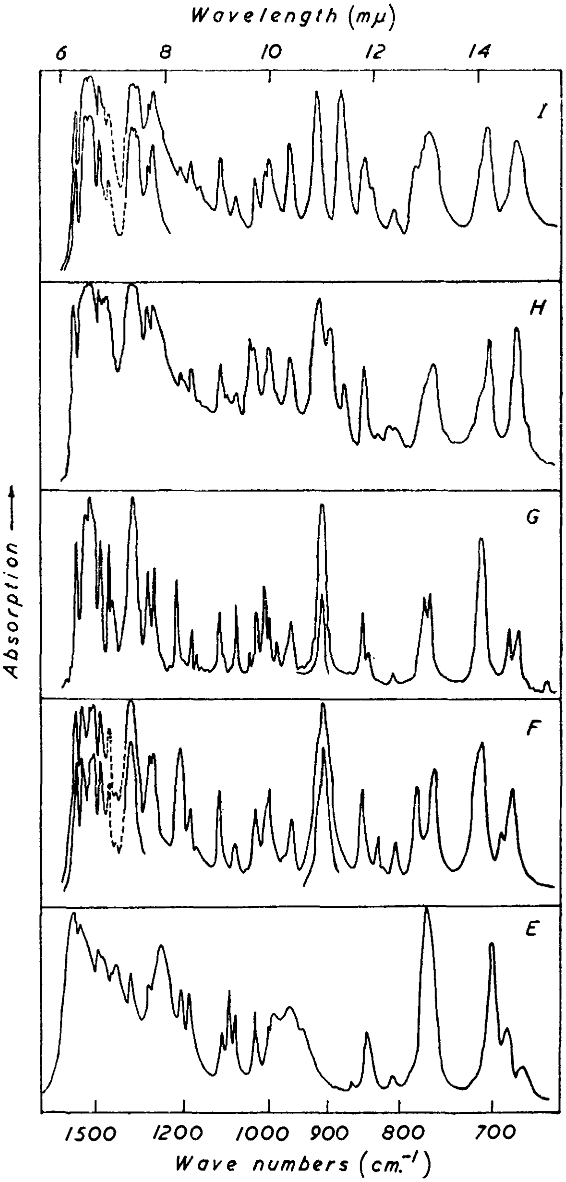

FIG. 2. *Spectra of benzoylacetone and* UO_2 *complexes:*

(*E*) Benzoylacetone.
(*F*) $UO_2(benzac)_2,NH_3$.
(*G*) $UO_2(benzac)_2,C_5H_5N$.
(*H*) $UO_2(benzac)_2,2{\cdot}5H_2O$.
(*I*) $UO_2(benzac)_2$.

Hence the problem of the structure of the uranyl radical cannot be considered to be satisfactorily solved.

The complexes here examined, containing water, ammonia, or pyridine of crystallisation, show a very strong band at about 910 cm.$^{-1}$ (Figs. 1, 2, 3) whose position is as follows:

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[14] Dicke and Duncan, " Spectroscopic Properties of Uranium Compounds, National Nuclear Energy Series, Division III, Vol. 2, McGraw-Hill Book Company, Inc., New York, 1949; Seaborg and Katz, " The Actinide Elements," National Nuclear Energy Series, Division IV, Vol. 14 A, McGraw-Hill Book Company, Inc., New York, 1954, pp. 165, 319.

in the complexes of acetylacetone it is between 925 and 910 cm.$^{-1}$, in those of benzoylacetone about 910 cm.$^{-1}$, and in those of dibenzoylmethane between 913 and 900 cm.$^{-1}$. It can be attributed to ν_3. In the acetylacetone complexes a second band, of low intensity, is present in the region 830—828 cm.$^{-1}$. Comparison with the spectra of the compounds $UO_2(OAc)_2,2H_2O$ and $UO_2(NO_3)_2,6H_2O$ (Fig. 5) showed that in the latter, in addition to the band ν_3, one can observe also a second band of very low intensity at 864 and 836 cm.$^{-1}$ which was attributed to the ν_1 vibration of the uranyl group.[4] This allows us to attribute the weak band of the acetylacetone complexes at 830—828 cm.$^{-1}$ to ν_1 vibration.

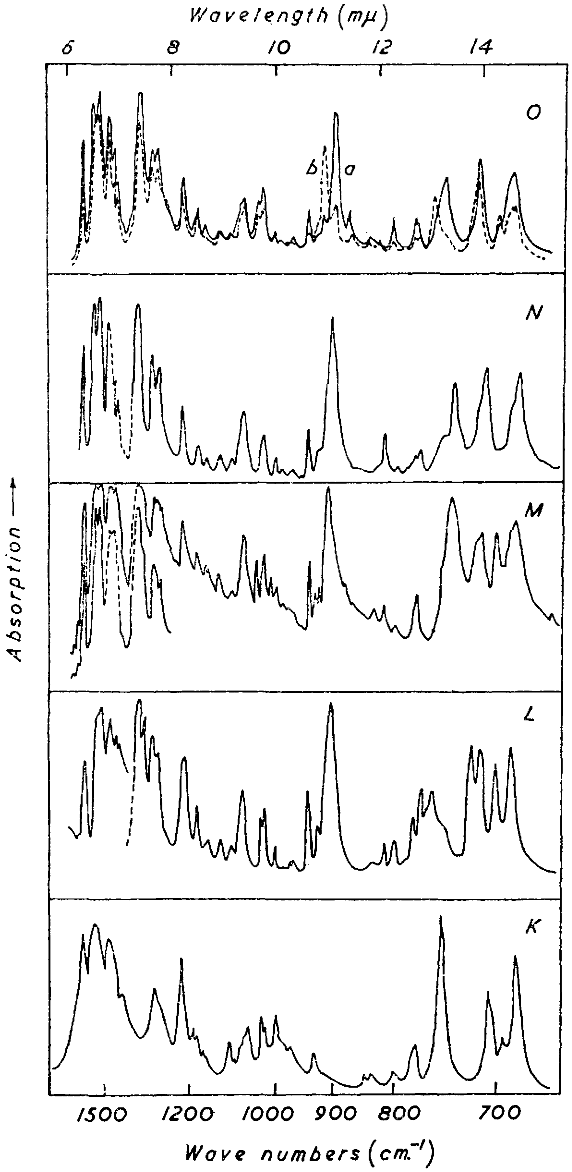


FIG. 3. *Spectra of dibenzoylmethane and* UO_2 *complexes*:

(*K*) Dibenzoylmethane.
(*L*) $UO_2(dimet)_2,NH_3$.
(*M*) $UO_2(dimet)_2,C_5H_5N$.
(*N*) $UO_2(dimet)_2,H_2O$.
(*O*) $UO_2(dimet)_2,2{\cdot}5H_2O$.

In the complexes of benzoylacetone and dibenzoylmethane the complexity of the spectra and the presence of absorption maxima of the ligands in the 860—830 cm.$^{-1}$ region do not allow us to ascertain the presence of the ν_1 band.

The anhydrous complexes with benzoylacetone and dibenzoylmethane show two bands each: at 915 and 887 cm.$^{-1}$ and at 920 and 886 cm.$^{-1}$ respectively (Figs. 2, 4). The spectra of two different samples of the latter were examined: one was obtained by double recrystallisation of the hydrate from benzene and ligroin, and the other by dehydration of the hydrated product under vacuum as described previously.[10] The spectra were practically identical.

These two bands can be attributed to ν_3 and ν_1 vibrations. It is noticeable however that: (*a*) the separation between the two frequencies, 28 and 34 cm.$^{-1}$ respectively for the complexes of benzoylacetone and dibenzoylmethane, is about half the theoretical value of 70 cm.$^{-1}$; (*b*) the theory predicts that the intensity of ν_3 should be much greater than that of ν_1, whereas we find that in our compounds both bands have practically equal intensity.

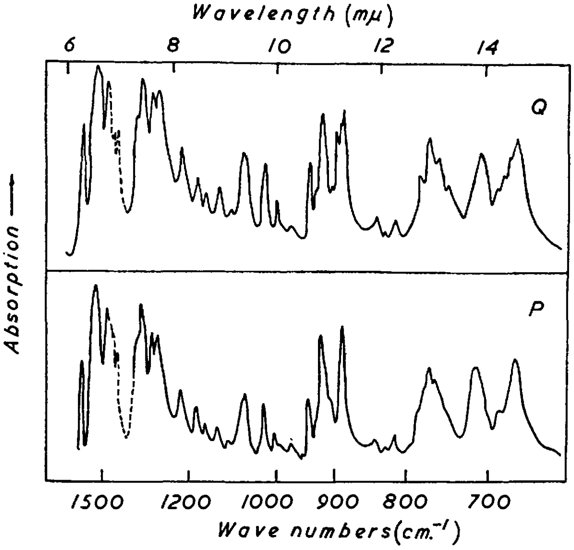
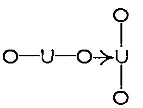


FIG. 4. *Spectra of* UO$_2$(dimet)$_2$:
(*P*) *Sample obtained by dehydration at* 100° in vacuo.
(*Q*) *Sample obtained by crystallisation from benzene.*

An explanation of this fact can be found in the modified crystal field of the anhydrous complexes. In these compounds, in fact, the " surroundings " of the UO$_2$ group differ from that in other complexes and it is probable that the aromatic groups of the ligands are nearer to the uranyl group, in the absence of molecules of water, ammonia, or pyridine in the crystal. Therefore it is conceivable that the interaction of these organic groups with the uranyl group may change the configuration or influence the polarisability of this group, altering the positions and the relative intensities of the absorption maxima and giving rise to new frequencies at 886 and 876 cm.$^{-1}$. An analogous change of the spectrum of uranyl sulphate trihydrate was observed by Sevcenko and Stepanov [7] on dehydration of this salt.*

On the basis of these results no definitive conclusions can be drawn about the form of the uranyl group in the complexes here examined. These results can probably be considered in agreement with the concept of an almost linear uranyl group disturbed by a strong local field, mainly in the case of anhydrous complexes. In the last case, however, a bent form for the uranyl radical cannot be excluded.



$$\mathrm{O{-}U{-}O{\rightarrow}\overset{\displaystyle O}{\underset{\displaystyle O}{U}}}$$

* The authors are grateful to a Referee for suggesting an alternative explanation for the changes occurring near 11 μ on dehydration of hydrated dibenzoylmethane and benzoylacetone complexes, and the behaviour of uranyl sulphate trihydrate on dehydration. It is suggested that the removal of co-ordinated water might allow an oxygen atom of one uranyl group to co-ordinate to the uranium atom of another uranyl group, *e.g.*, as in the inset. This would certainly alter the UO$_2$ frequencies and bond intensities while retaining the linear or near-linear structure of the group.

Absorption of Water.—Water vapour shows three fundamental bands: at 3756, 3652, and 1595 cm.$^{-1}$;[15] the first two correspond to stretching vibrations and the third to a bending vibration. All the hydrated complexes absorb between 3570 and 3100 cm.$^{-1}$ (see Fig. 6). This absorption is clearly due to the presence of water because the diketones and the anhydrous complexes do not absorb in this region. In some cases sharp bands are observed, while in others there is a broad ill-defined band.

FIG. 5.

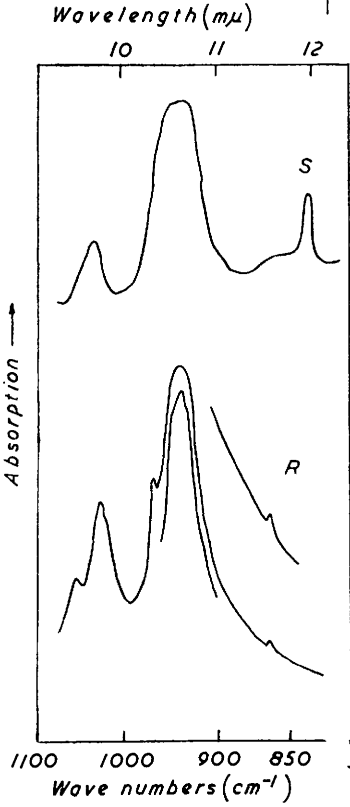


FIG. 6.

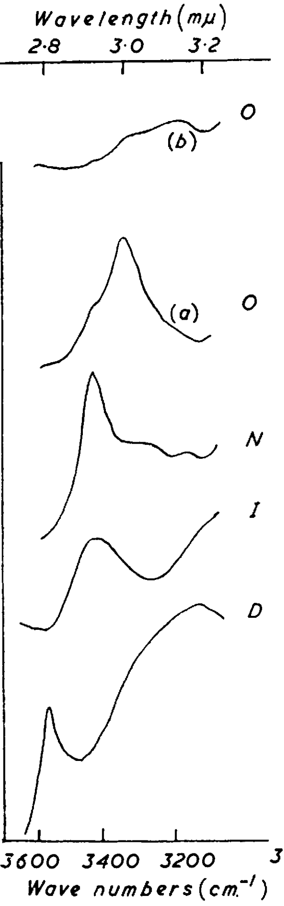


FIG. 7.

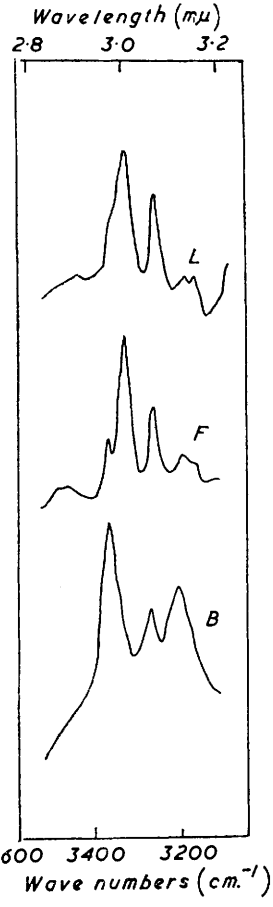


FIG. 5. *Spectra of (R) uranyl acetate and (S) uranyl nitrate.*

FIG. 6. *Spectra of hydrated uranyl–diketone complexes in the absorption region of water.*

FIG. 7. *Spectra of ammoniated uranyl–diketone complexes in the absorption region of ammonia.*

Absorption in this region is due to O–H stretching. The fact that there are no frequencies higher than 3570 cm.$^{-1}$ shows that the O–H stretching vibrations are not completely free, probably because of hydrogen bonding. The very broad band observed in many cases is an indication that, in all probability, different types of hydrogen bonding are present because of the presence of many oxygen atoms in the carbonyl groups. In some cases one observes that different samples of the same compound, from different preparations and with correct analyses, absorb differently in this region. This is so with

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[15] Herzberg, "Molecular Spectra and Molecular Structure: Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand Co., New York, 1947.

curves (*a*) and (*b*) of the complex with dibenzoylmethane. The peak on the high-frequency side in curve (*a*) can be attributed to interstitial water, less strongly bound than the other water molecules.

The spectrum of water in the $2\frac{1}{2}$ hydrate of the complex of dibenzoylmethane varies even with the manipulation of the sample. The lack of reproducibility in the 3μ region is not observed in the monohydrate of the same complex. This leads to the supposition that the molecules of water in the former complex are not all bound equally strongly.

These variations of the O–H stretching band are accompanied by marked variations of the UO_2 band at about 910 cm.$^{-1}$ as shown by the spectra of two different samples (*a*) and (*b*) of the same $2\frac{1}{2}$ hydrate in Fig. 3 (curve *O*). This interaction between the UO_2 group and the water molecules leads to the conclusion that the UO_2 radical is closely bonded to at least a part of the crystal water. This supports the hypothesis of McKay and his co-workers,[9] and analogous ideas put forward in previous investigations (Parts I and II). According to these views, the uranyl group, in its inorganic salts and its complexes with β-diketones, tends to co-ordinate molecules of water. The first sphere of co-ordinated water, in turn, binds further water molecules through hydrogen bonding. Moreover, the spectroscopic data do not allow an estimate to be made of the strength of the bond between water and the central uranium atom. The presence of co-ordinate bonds between uranium and water molecules should give rise to new absorption bands corresponding to new modes of vibration (*e.g.*, rocking, etc.) of the water bonded to the central uranium atom. However, these bands are expected in the 10—14 μ region,[16] and here the presence of other strong absorption bands does not permit of their identification. Also, the 1595 cm.$^{-1}$ band of water is not identifiable owing to the complexity of the spectrum in this region, due to absorption of various functional groups such as carbonyl, phenyl, and furan rings.[17]

Absorption of Ammonia.—Gaseous ammonia shows two bands in the 3μ region: 3337 and 3450 cm.$^{-1}$. In Fig. 7 are drawn the absorption spectra, in this region, of the complexes studied by us. These curves show three main absorption maxima between 3166 and 3367 cm.$^{-1}$, *i.e.*, shifted towards lower frequencies with respect to those in gaseous ammonia. With the benzoylacetone and dibenzoylmethane complexes the first and third peaks appear to be split and shifted towards lower frequencies. These bands indicate that the nitrogen atom is co-ordinated to the uranium atom. The frequency shifts observed are of the same order of magnitude as those observed in complex ammines of the " ionic " type, *e.g.*, $[Co(NH_3)_6]Cl_2$ and $[Ni(NH_3)_6]Cl_2$, but lower than those observed in " covalent " complexes, *e.g.*, $[Co(NH_3)_6]Cl_3$ and $[Cr(NH_3)_6)Cl_3$.[18] This would lead to the conclusion that the U–N bond in these complexes is only partially covalent. A definite conclusion, however, cannot be reached because the shift toward lower frequencies in the NH_3 bands could be attributed chiefly to the presence of hydrogen bonds in the crystal.

The great complexity of the spectra does not readily allow the assignment of the many other bands observed to the functional groups present, which is, however, beyond the scope of the present investigation.

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[16] Fujita, Nakamoto, and Kobayashi, *J. Amer. Chem. Soc.*, 1956, **78**, 3963.
[17] Holtzclaw, jun., and Collman, *J. Amer. Chem. Soc.*, 1957, **79**, 3318.
[18] Svatos, Curran, and Quagliano, *ibid.*, 1955, **77**, 6159.