Preparation and Infrared Spectroscopic Characterization of Some (Oxydiacetato)uranyl(VI) Complexes

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Polymeric complexes, $[UO_2(oda)]_n$ (oda = oxydiacetate, $O_2CCH_2OCH_2CO_2^{2-}$, $n = \infty$), have been prepared, from the reaction of uranyl(VI) ions and oxydiacetic acid or its disodium salt, and characterized, mainly by i.r. spectroscopy. The complex $Na_2[UO_2(oda)_2],nH_2O$ (n = 2 or 3) was obtained when an excess of the ligand was used in the reaction. In the presence of pyridine *N*-oxide(Opy), both monomeric $[UO_2(oda)(Opy)_2]$ and polymeric $[UO_2(oda)(Opy)]_n$ ($n = \infty$) complexes were obtained.

THE interaction of the UO_2^{2+} ion with polyfunctional ligands containing carboxylato-groups and other oxygen and nitrogen donor groups has been investigated by many authors.[1] The main interest has been in the determination of the stability constants. There is evidence for the existence of complex species of different composition in solution, suggesting the possibility of obtaining in the solid state complexes of different stoicheiometry and structure. Only a few such complexes have been isolated so far and, for some, structures have not been fully established.[1] In this respect, ligands which give rise to species containing five-membered rings appear to be of particular interest.[2,3]

Our attention was thus directed to the anion of oxydiacetic acid which has two carboxyl groups and an ether oxygen atom in the α position to both of them. This ligand could co-ordinate to a uranium atom through the ether oxygen atom and the oxygen atoms of the carboxylato-groups. There is also the possibility of formation of polymeric species as in the case of the $[(UO_2)_2(C_2O_4)_3]^{2-}$ ion.[4]

EXPERIMENTAL

The reagents were commercial products, used without further purification, or were prepared by standard methods.

Preparations.—$[UO_2(oda)]_n$ (oda = *Oxydiacetate*, n = ∞) (I). This complex was prepared by the addition of $UO_2(NO_3)_2,6H_2O$ (1 mmol), dissolved in water (*ca.* 10 ml), to an equimolar amount of H_2oda or Na_2(oda), in a few millilitres of the same solvent. The mixture was set aside for several hours and the yellow crystals which separated were filtered, washed with water, then with methanol and ether. The *complex* obtained is anhydrous. Yield 75% {Found: C, 11·6; H, 1·1; U, 59·3. $[UO_2(oda)]$ requires C, 11·9; H, 0·95; U, 59·2%}.

$[UO_2(oda)]_n$, n = ∞ (II). This complex was prepared by the addition of a methanolic solution of $UO_2(NO_3)_2,6H_2O$ (1 mmol, 5 ml of solvent) to a solution containing a stoicheiometric amount of H_2oda or Na_2(oda) in the same solvent (1 mmol, 20 ml). A yellow precipitate was formed immediately; it was washed with methanol and ether. The *complex* is anhydrous. Yield 70% {Found: C, 11·8; H, 1·1; U, 58·4. $[UO_2(oda)]$ requires C, 11·9; H, 0·95; U, 59·2%}.

$Na_2[UO_2(oda)_2],nH_2O$ (n = 2 or 3) (III). This complex was prepared by the addition of a solution of Na_2(oda) to a solution of uranyl(VI) nitrate in the mole ratio oda : UO_2^{2+} =

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[1] L. Cattalini, S. Degetto, U. Croatto, and E. Tondello, *Inorg. Chim. Acta Rev.*, 1971, **5**, 19 and refs. therein.

[2] L. Cattalini, S. Degetto, L. Baracco, and G. P. Marangoni, *Atti Accad. Peloritana*, 1971, **51**, 267.

[3] K. S. Rajan and A. E. Martell, *J. Inorg. Nuclear Chem.*, 1964, **26**, 789.

[4] N. W. Alcock, *Chem. Comm.*, 1968, 1327.

2 : 1. When the solvent was methanol, the complex precipitated immediately and quantitatively as a fine yellow powder. When the reaction was carried out in water, in which this complex is very soluble, addition of ethanol or methanol was needed in order to initiate precipitation (unless very high concentrations were used). The *complex* contains at least two molecules of water of crystallization {Found: C, 15·6; H, 1·6; U, 37·7. $Na_2[UO_2(oda)_2],2H_2O$ requires C, 15·5; H, 1·95; U, 38·6%}.

$UO_2(oda)(Opy)_2]$ (Opy = *Pyridine* N-*oxide*) (IV). This complex was prepared in two different ways. In the first method a mixture of complexes (I) and (II) were added to a ten-fold excess of pyridine *N*-oxide in methanol. After 24 h the complexes had reacted completely and deep yellow crystals of complex (IV) were obtained. These were filtered, washed with small volumes of methanol then with ether, and dried. In the second method the *complex* was obtained on dissolution of (I) or (II) in boiling water followed by the addition to the cooled solution of an excess of the ligand {Found: C, 27·9; H, 2·4; N, 4·6; U, 40·6. $[UO_2(oda)(Opy)_2]$ requires C, 28·4; H, 2·4; N, 4·5; U, 40·2%}.

$[UO_2(oda)(Opy)]_n$ ($n = \infty$) (V). This *complex* was prepared following the above procedure (first method), but using a much smaller excess of pyridine *N*-oxide, two or three times the stoicheiometric amount {Found: C, 21·5; H, 1·9; N, 2·9; U, 47·8. $[UO_2(oda)(Opy)]$ requires C, 21·75; H, 1·8; N, 2·8; U, 47·8%}.

All i.r. spectra of the complexes were recorded on KBr pellets in the region 4000—300 cm^{-1} on a Perkin-Elmer 621 spectrophotometer. Conductivity data were measured on aqueous solutions of the complexes using a LKB type 3216B bridge. C, H, and N analyses were performed by the microanalytical laboratory of the University of Padua. Uranium was determined gravimetrically as U_3O_8.

RESULTS AND DISCUSSION

The reaction of an aqueous solution of $UO_2(NO_3)_2,6H_2O$ and oxydiacetic acid (H_2oda) or its disodium salt, in the mole ratio 1 : 1, yielded two different types of complex, depending on the concentrations of the reactants. Dilute solutions resulted in the formation of a complex $[UO_2(oda)]_n$ ($n = \infty$) (I); concentrated solutions gave a complex (II) of the same stoicheiometry, but with a different i.r. spectrum. If the solvent used was methanol, compound (II) was generally obtained; however, if very dilute solutions of the starting materials were allowed to crystallize slowly, complex (I) could be isolated even with this solvent. Both complexes are insoluble in all solvents. The composition, insolubility, and absence of co-ordinated solvent molecules, as shown by i.r. spectra, strongly suggest that these species possess a polymeric structure. From uranyl(VI) nitrate and Na_2(oda) in the mole ratio 1 : 2, both in water and in methanol, the complex $Na_2[UO_2(oda)_2],nH_2O$ ($n = 2$ or 3) was obtained ($\Lambda = 170\ \Omega^{-1}\ cm^2\ mol^{-1}$ in 10^{-3}M-solution at 21 °C).

The polymeric structure of complexes (I) and (II) was destroyed by boiling water, yellow solutions, being obtained which were nonconducting. Presumably neutral species $[UO_2(oda)],xH_2O$ ($x = 2$ or 3) are formed in which molecules of solvent complete the co-ordination sphere of the UO_2^{2+} ion. When a large excess of pyridine *N*-oxide (Opy) was added to these solutions, the complex $[UO_2(oda)(Opy)_2]$ (IV) was formed. This complex could also be obtained directly from (I) and (II) in a concentrated methanolic solution of pyridine *N*-oxide. An intermediate complex containing only one molecule of pyridine *N*-oxide, $[UO_2(oda)(Opy)]_n$ ($n = \infty$) (V), was also isolated. This reacts with another molecule of pyridine *N*-oxide to give complex (IV). Complex (V) dissolves slightly in cold water; this fact does not conflict with a polymeric structure in the solid state, but indicates that attack by water to give a monomeric species is easier with this complex than with complexes (I) and (II).

I.r. Spectra.—For all the complexes isolated, the asymmetric and symmetric stretching frequencies of the ether group, which occur at 1138 and 1053 cm^{-1} in the disodium salt of the ligand, were slightly, but significantly, shifted towards lower wavenumbers. The two bands were equally intense, whereas in the free ligand that at higher frequency is the more intense. These differences suggest co-ordination of the ether oxygen atom to the uranium atom; a lowering in the stretching frequencies of the C–O–C group in co-ordinated ethers is generally acknowledged.[5]

The most significant information, on the geometry of these complexes comes, however, from analysis of the carboxyl group absorption region. Stretching frequencies of this functional group are closely related to the way in which it is co-ordinated to the metal atom.[6] In the i.r. spectrum of complex (III) (Figure) there were two absorption bands in the C–O stretching region at 1670, 1615 and 1420 cm^{-1}. The separation between asymmetric and symmetric stretching bands of this group was much higher than that found in the free oxydiacetate anion and the higher-frequency band was much more intense. The relative position of the two absorption bands suggests that one of the C–O bonds has taken up more double-bond character on co-ordination; therefore we conclude that the oxydiacetate anion is tridentate in this complex, having two free carboxylic oxygen atoms.[7,8] A co-ordination number of six, in the equatorial plane, is achieved by the uranyl(VI) ion. In complex (IV), the C–O stretching frequencies occurred at 1660 and 1390 cm^{-1}; thus the co-ordination of the oxydiacetate ligand is identical to that suggested for complex (III). The co-ordination number, in the equatorial plane, is made up to five by two pyridine *N*-oxide molecules.

The i.r. spectrum of complex (I) showed in the C–O stretching region, a very broad and intense band at 1565 cm^{-1} and two quite sharp bands at 1481 and 1440 cm^{-1}

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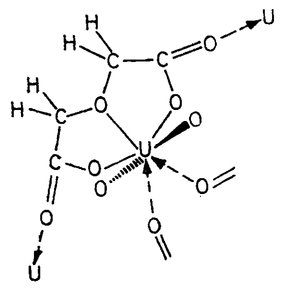
[5] G. Pregaglia, G. Mazzanti, and D. Morero, *Ann. Chim. (Italy)*, 1959, **49**, 1784; M. J. Taylor, *J. Chem. Soc.* (*A*), 1967, 1462; H. Wieser and P. J. Krueger, *Spectrochim. Acta*, 1970, **26***A*, 1349.

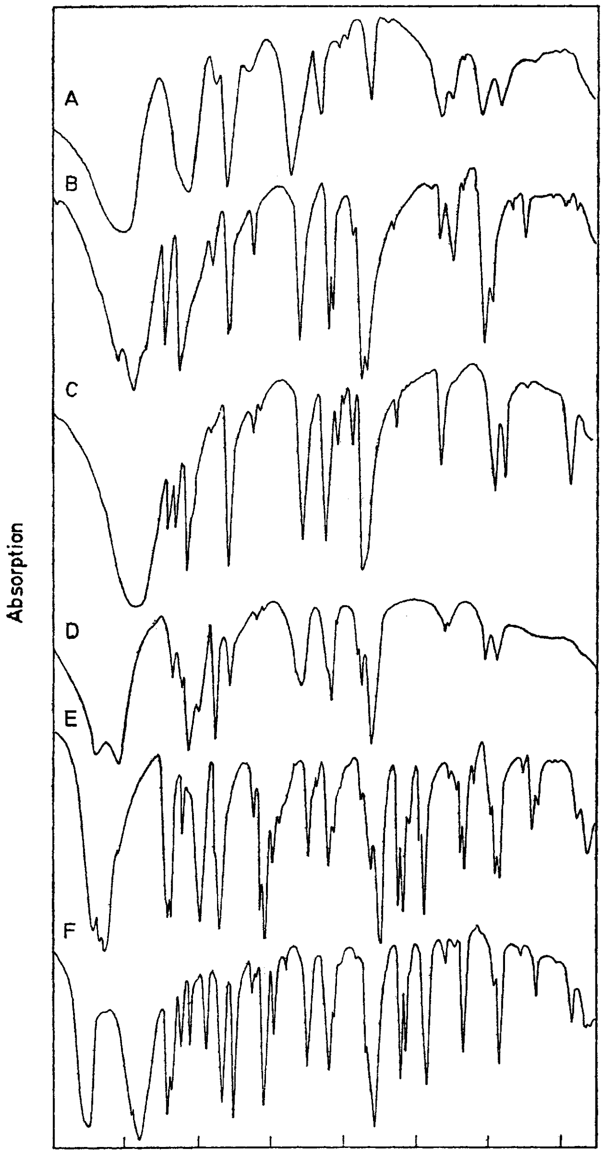
[6] A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1962, 5262.

[7] D. V. Naik and C. Curran, *Inorg. Chem.*, 1971, **10**, 1017.

[8] J. F. Jackovitz, J. A. Durkin, and J. L. Walter, *Spectrochim. Acta*, 1967, **23***A*, 67.

of much lower intensity. The only complication comes from the presence of CH_2 groups which have a deformation vibration in this region. We believe that the band at 1440 cm^{-1} is assignable to the symmetric $-\mathrm{C}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}$ stretch or, at least, it consists of this stretch plus the methylene deformation. The separation between the two stretching frequencies is very close to that in the free oxydiacetate anion, but there is a drastic change in the relative intensities. If the carboxylato-groups were monodentate, we should have expected a higher frequency for the antisymmetric stretch (above **1600** cm^{-1}, the value for the free oxydiacetate anion). On the other hand, since the ether oxygen atom is co-ordinated, the geometry of the oxydiacetate ligand requires that the carboxyl groups be only monodentate towards the same metal ion. The only way in which all four carboxylato-group oxygen atoms may be involved in co-ordinate bond to the uranium atom is then through a polymeric structure. One possibility is shown below, where carboxylato-group oxygen atoms not engaged in formation of the first monomeric units, fill the co-ordination spheres of adjacent uranium atoms. This structure, based on i.r. spectral data, has been proven by *X*-ray analysis.[9] The origin of the band at 1481 cm^{-1} in the i.r. spectrum of complex (I) is rather uncertain. The frequency appears to be higher than expected for a CH_2 group adjacent to a carbonyl group,[10] and it could be caused by coupling between the two C–O bonds employed in formation of the two five-membered rings.





I.r. absorption spectra of disodium oxydiacetate and (oxydiacetato)uranyl(VI) complexes: A, $Na_2(oda)$; B, $[UO_2(oda)]_n$ (I); C, $[UO_2(oda)]_n$ (II); D, $Na_2[UO_2(oda)_2],xH_2O$ (III); E, $[UO_2(oda)(Opy)_2]$ (IV); and F, $[UO_2(oda)(Opy)]_n$ (V) ($n = \infty, x = 2$)

The spectrum of complex (II), which has the same composition as that of (I), has some characteristics which indicate a different structure to that of (I). In the C–O stretching region there was a strong broad band at 1575 cm^{-1} and much weaker sharp bands at 1480, 1460, and 1430 cm^{-1}. To explain the occurrence of these different bands, one can assume that in complex (II) some carboxylato-groups act as bidentate ligands towards the uranium atom; although formation of five-membered rings seems to be generally favoured, the fast precipitation, in this case, could prevent the oxydiacetate ligand from attaining its usual configuration around the metal atom. The presence of a carboxylato-group acting as a bidentate ligand towards the same uranium atom could give rise to two peaks of the same intensity, with a separation of *ca.* 70 cm^{-1}.[11] In complex (II), however, the higher-frequency component would be completely obscured by the broad band at 1575 cm^{-1}; the other component could be identified with one or other of the absorption bands at 1480 and 1460 cm^{-1}. Further significant differences between the spectra of complexes (I) and (II) have been found in the bending region, as shown in the Table.

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[9] G. Bombieri, E. Forsellini, R. Graziani, L. Magon, and G. Tomat, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 1003.

[10] L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 1966, p. 23.

[11] L. H. Jones, *J. Chem. Phys.*, 1955, **23**, 2105.

Complex (V) exhibited a sharp band at 1700 cm^{-1} and a rather broad intense band at 1560 cm^{-1}. The structure of (V) can be derived from that of complex (I) by introducing a molecule of pyridine *N*-oxide, which fills a co-ordination site on the uranium atom. Half of the carboxylato-group oxygen atoms, which formed the polymeric structure, are now free and the corresponding C–O bonds, having become nearly pure double bonds, give rise to the 1700 cm^{-1} band. The other half are still co-ordinated and the related C–O linkages are responsible for the broad band at 1560 cm^{-1}. Unfortunately the presence of the ligand pyridine *N*-oxide made it difficult to locate the lower C–O bands.

Assignments of characteristic i.r. frequencies (cm^{-1}) of the oxydiacetate ion and its UO_2^{2+} complexes

Assignments \ Complex	$Na_2(oda),H_2O$	$Na_2(oda)$ [a]	(I)	(II)	(III)	(IV)	(V)
CO_2 asym. stretch	1620vs,br	1600vs,br	1613w 1565vs,br	1570vs,br	1670vs,br 1615vs,br	1660vs	1700s 1560vs,br
Other bands in the region of C–O stretching modes			1481ms [b]	1480w [b] 1460w [b]			
CO_2 sym. stretch	1420s	1418s	1440ms	1430m	1420s	1390ms	*c*
COC asym. stretch	1143s	1138s	1109ms	1113ms	1119m	1092m	1096m
COC sym. stretch	1063m	1053m	1034ms 1026m	1046ms	1031m	1037m	1036m
OUO asym. stretch			930s [d] 944s [d]	940s	917s	895s	913s
δ(C=O): in-plane C–O bending	726w	726mw 700w	718w 691mw	730mw	710w,br	*c*	*c*
π(C=O): out-of-plane C–O bending	562mw	614mw 558mw	604ms 588w	585mw 555mw	604w 572w	*c*	*c*

[a] The i.r. spectra of $Na_2(oda),H_2O$ and anhydrous $Na_2(oda)$ show some differences; all comparisons with such frequencies are referred to the anhydrous salt. [b] These absorption bands could be assigned to C–O stretching modes; however care is needed as methylene deformation vibrations occur in the same region. [c] Assignment is not possible because of overlapping with pyridine *N*-oxide bands. [d] The near proximity of $\nu_{asym}(OUO)$ and ν(C–C) (occurring at 920 cm^{-1} in the free oxydiacetate anion) makes assignment of these two bands difficult.

The asymmetric O–U–O stretching frequency appeared at 940 cm^{-1} in complexes (I) and (II), at *ca.* 915 cm^{-1} in the anionic complex (III) and in complex (V), and at 895 cm^{-1} in the monomeric pyridine *N*-oxide complex. It is to be noted that rather low O–U–O asymmetric stretching frequencies have already been found in complexes in which pyridine *N*-oxide is co-ordinated to the uranyl(VI) ion.[12]

CONCLUSIONS

We suggest that the driving force in the formation of complex species containing UO_2^{2+} and the oxydiacetate ligand lies in their different solubility. In aqueous solution, a likely intermediate for these reactions is that in which the ligand occupies three co-ordination sites of the UO_2^{2+} cation with solvent molecules filling the remaining positions. Formation of such an intermediate would be followed by replacement of the solvent molecules by unco-ordinated carboxylato-group oxygen atoms from adjacent molecules, thus giving rise to polymeric structures. This process can be reversed and the polymers can be destroyed by boiling water. The presence in the system of another ligand, the basicity of which is higher than that of the solvent, such as pyridine *N*-oxide or oxydiacetate in excess, permits the formation of stable monomeric species.

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[12] M. S. Subramanian and V. K. Manchanda, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3001.