U(VI) COMPLEXES OF OXINE AND DERIVATIVES

A. CORSINI[®], J. ABRAHAM and M. THOMPSON McMaster University, Hamilton, Ontario, Canada

(Received 19 August 1970. Accepted 8 October 1970)

Summary—Infrared bands due to the hydrogen-bonded +N—H \cdots O system in the oxine adduct of U(VI) have been identified and found to occur in the spectra of several newly prepared U(VI) adducts of oxine derivatives. Interligand steric effects in the U(VI) complexes of most 7-substituted oxines prevent the formation of the 1:3 adduct. Complexes of the type ML₁X, where X is a small co-ordinating species present in solution, are formed instead. With 2-substituted oxines, steric interactions between the 2-substituent and co-ordinated water result in destabilization of the complex and subsequent hydrolysis as the pH of the solution is raised. Experiments involving the use of [¹⁴C]-oxine were found to distinguish between co-ordinated and lattice-held oxine and are potentially valuable in studies of oxine adducts formed by other metal ions.

THE RED ADDUCT, $UO_2(C_9H_6NO)_2 C_9H_7NO$, formed between uranium(VI) and oxine (8-hydroxyquinoline) has been used in chemical analysis for several years.¹ Until recently, there had been some speculation about the manner in which the additional molecule of oxine (HOx) is bound. Suggestions^{2,3} that this molecule is an unco-ordinated crystal-lattice component conflicted with those⁴⁻⁸ that it is co-ordinated to the central uranium(VI) atom. A subsequent X-ray structure determination⁹ by Hall *et al.* showed that the extra molecule is indeed co-ordinated to the uranium(VI) atom, but through the phenolate oxygen only. In a recent communication,¹⁰ the present authors reported the location of the acidic proton in the adduct, and a series of new uranium(VI) complexes of HOx derivatives. Also, reference was made to a method involving the use of [¹⁴C]-HOx for investigating the nature of the adduct. In the present report we wish to provide the details of the communication and of the findings of more recent work.

Chemicals

EXPERIMENTAL

All common chemicals were of suitable purity for the intended purpose. $UO_2(NO_3)_3 \cdot 6H_3O$ (AnlaR grade, B.D.H.) was used without further purification. Oxine, 2-methyl- and 5-chloro-oxine were obtained commercially and purified by sublimation or recrystallization; 2,7-dimethyloxine was available in the laboratory. [¹⁴C]-Oxine was synthesized as described earlier.¹¹ Its specific activity was 3.6 mV sec⁻¹ mg⁻¹.* The following derivatives were synthesized by procedures in the literature: 2-n-butyl,¹³ 2-phenyl,¹³ 2-(2'-thienyl),¹⁴ 5-methyl,¹⁵ 5-phenyl,¹⁶ 5-acetyl,¹⁷ 5-nitro,^{18.19} 7-methyl,³⁰ and 7-phenyloxine.¹⁶

7-t-Butyloxine was synthesized by a Skraup-type reaction. 2-Amino-6-t-butylphenol (21 g) and glycerol (72 g) were condensed in concentrated sulphuric acid (22 ml) at 130-140° for 4 hr in the presence of 2-nitro-6-t-butylphenol (15 g) as an oxidant. The viscous reaction mixture was cooled, diluted with water, and the excess of oxidant removed by steam-distillation. After neutralization with sodium hydroxide, the mixture was steam-distilled to give 7-t-butyloxine. The product was purified by further steam-distillation and recrystallization from aqueous ethanol to yield white needles, m.p. 92-93°. The yield was 25%, calculated on the amount of amino compound taken. Calculated for $C_{19}H_{15}NO$: C, 77.58%; H, 7.51%; N, 6.96%. Found: C, 77.5%; H, 7.5%;

* Measurements of [¹⁴C]-activity were made by the "rate of drift" method which yields units of mV sec⁻¹ mg⁻¹ (see V. F. Raaen and G. A. Ropp, *Anal. Chem.*, 1953, 25, 174). Conversion into units of disintegrations sec⁻¹ mg⁻¹ was not necessary.

N, 7.0%. The compound was further characterized by infrared, mass and NMR spectroscopy. All spectra exhibited the expected features. The starting compound, 2-amino-6-t-butylphenol, was prepared by nitration of 2-t-butylphenol,^{s1} followed by hydrosulphite reduction to the amine.

Synthesis of uranium(VI) complexes

The complexes were precipitated from aqueous solution or from 40% v/v acetone-water solution when ligands of low aqueous solubility were used. The pH was adjusted by hydrolysis of urea, or by addition of aqueous ammonia or dilute sodium hydroxide solution.

Precipitation by urea hydrolysis. $UO_a(Ox)_a$ HOx was prepared by the procedure of Moeller and Wilkins.²² The following procedure was used for the preparation of the uranium(VI) complexes of 5-Me (brick-red), 5-Ph (brick-red), 5-NO₂ (yellow), 5-Ac (brick-red), 7-Me (dark brown) and 7-PhOxH (orange-brown). $UO_a(NO_a)_a$ 6H₂O (0.20 mmole) dissolved in 50 ml of water containing 2 drops of concentrated nitric acid was warmed to 70-80° and the appropriate reagent derivative (0.72 mmole, but 1.1 mmole of 5-AcOxH) dissolved in 2 ml of glacial acetic acid was added slowly with stirring. After the addition of urea (5.5 g), the mixture was heated to boiling, placed on a steambath for 5 hr, with periodic stirring, and then filtered (hot). The pH of the cooled filtrate was 5.8-6.0. The precipitate was washed once with 90% ethanol and 3 times with hot water and was dried overnight on a water-aspirator and then at 100° for 2 hr.

Precipitation by aqueous ammonia. The adduct of 2-MeOxH was prepared by the procedure of Phillips et al.²³ The method for the preparation of the 7-Me (dark brown) and 2,7-diMeOxH (brickred) complexes was similar to the urea procedure except that the pH was adjusted (to 7) by the dropwise addition of 4M ammonia, and the mixture was not boiled. The 7-t-Bu (red-brown) and 5-ClOxH (orange-brown) complexes were prepared as follows. UO₂(NO₃)₂·6H₃O (0·20 mmole) was dissolved in 60 ml of water containing 2 drops of concentrated nitric acid and the solution was warmed to 60°. The reagent (0·72 mmole) dissolved in 40 ml of acetone was added slowly, followed by careful addition of 4M ammonia to adjust the pH to 7. The solution was cooled to 40–50°, and the precipitate was then filtered off and washed and dried as above.

Precipitation by dilute sodium hydroxide solution. The 7-Me and 2,7-diMeOxH complexes were precipitated by the previous procedure except that 0.2M sodium hydroxide was used in place of 4M ammonia.

Thermal conversion into 1:2 complexes

The adducts of 2-MeOxH and the 5-substituted derivatives were converted into the corresponding bis (1:2) compounds by heating a few hundred mg of each adduct at $210-225^{\circ}$ (oil-bath) for 3-4 hr *in vacuo* (0.13 mbar). The sublimed reagent was collected as a compact deposit in the initial portion of a U-tube immersed in a solid-CO₂ bath. In general, the thermal decomposition products were black. All complexes containing ammonia, water or acetone were also converted into the corresponding 1:2 compounds (black) by the same procedure. Only the products from UO₂(7-MeOx)₂·H₂O and UO₂(7-t-BuOx)₂·OC(CH₃)₂ were analysed.

Derivative Formula	Dan 1	Calculated (%)				Found (%)					
	С	н	N	Cl	U	С	H	N	Cl	U	
5-MeOxH	UO ₂ (C ₁₀ H ₈ NO) ₂ ·C ₁₀ H ₉ NO	48.33	3.38	5.64		31.93	48 •4	3.9	5.5		32.0
5-PhOxH	UO ₂ (C ₁₅ H ₁₀ NO) ₂ ·C ₁₅ H ₁₁ NO	58.01	3.35	4.51		25.55	57.9	3.4	4.4		25.1
5-NO₂OxH	UO ₂ (C ₂ H ₅ N ₂ O ₃) ₃ ·C ₂ H ₆ N ₂ O ₃	38.67	1.93	10.03		28.38	37.6	2.0	10.0		29.1
5-AcOxH	$UO_2(C_{11}H_1NO_2)$, $C_{11}H_1NO_2$	47.74	3.04	5.06		28.67	48 .8	2.9	4.9		27.6
7-PhOxH	UO ₂ (C ₁₅ H ₁₀ NO) ₂ ·C ₁₅ H ₁₁ NO	58 ·01	3.35	4.51		25.55	58.3	3.3	4.6		25.1
7-MeOxH	UO ₂ (C ₁₀ H ₈ NO) ₂ ·NH ₃ *	39.81	3.17	6.96		39.45	39.6	3.0	6.4		39-4
7-MeOxH	UO ₂ (C ₁₀ H ₈ NO) ₂ ·H ₂ O	39.74	3.00	4.64		39.38	39.8	3.3	4.8		38.81
							39.3	3.2	4.6		39·61
2,7-diMeOxH	$UO_2(C_{11}H_{10}NO)_2 \cdot H_2O$	41·78	3.51	4.43		37.63	42.5	3.7	4·3		36.1†
							43·2	3.7	4·2		35-0±
5-ClOxH	UO ₂ (C ₂ H ₅ NOCl) ₂ ·C ₂ H ₅ NOCl	40.19	2.00	5.21	13.18	29.50	40.2	1.9	5.2	13.05	29.4
7-t-BuOxH	UO ₂ (C ₁₂ H ₁₄ NO) ₂ ·OC(CH ₂) ₂	47.81	4.70	3.84		32.67	49.7	4.8	4.3		30-1
7-MeOxH	$UO_2(C_{10}H_8NO)_3$	40.96	2.76	4.78		40.58	40.6	3.0	5.1		41.6
7-t-BuOxH	UO ₂ (C ₁₃ H ₁₄ NO) ₂	46.57	4·21	4·18		35.50	45 ⋅8	4∙0	4.5		35.7
7-MeOxH 2,7-diMeOxH 5-ClOxH 7-t-BuOxH 7-MeOxH 7-t-BuOxH	$UO_{2}(C_{10}H_{8}NO)_{2}\cdot H_{2}O$ $UO_{2}(C_{11}H_{10}NO)_{2}\cdot H_{2}O$ $UO_{3}(C_{8}H_{8}NOC)_{2}\cdot C_{8}H_{8}NOC $ $UO_{3}(C_{12}H_{14}NO)_{2}\cdot OC(CH_{9})_{2}$ $UO_{3}(C_{10}H_{8}NO)_{3}$ $UO_{2}(C_{13}H_{14}NO)_{2}$	39·74 41·78 40·19 47·81 40·96 46·57	3.00 3.51 2.00 4.70 2.76 4.21	4.64 4.43 5.21 3.84 4.78 4.18	13-18	39·38 37·63 29·50 32·67 40·58 35·50	39.8 39.3 42.5 43.2 40.2 49.7 40.6 45.8	3·3 3·2 3·7 3·7 1·9 4·8 3·0 4·0	4·8 4·6 4·3 4·2 5·2 4·3 5·1 4·5	13.05	38.8† 39.6‡ 36.1† 35.0‡ 29.4 30.1 41.6 35.7

TABLE I

* A modified Kjeldahl method gave 2.4% NH₃ (calculated, 2.83%).

† Precipitated by aqueous ammonia.

[‡] Precipitated by dilute sodium hydroxide solution.

U(VI) complexes of oxine and derivatives

Infrared spectra

Infrared spectra were recorded with a Beckman IR-5 spectrophotometer. The samples were prepared as mulls in spectrally-pure hexachloro-1,3-butadiene. To obtain suitable intensities of the 2050 and 2650 cm⁻¹ adduct bands, approximately 2-3 times the quantity of solid usually employed for mull preparation was used.

Exchange between UO₁(Ox)₂·HOx and [¹⁴C]-HOx in solution

To 5.0 ml of 1,2-dichloroethane containing 52 mg (0.36 mmole) of [¹⁴C]-HOx (specific activity, 3.6 mV sec⁻¹ mg⁻¹) were added 126 mg (0.18 mmole) of UO₂(Ox)₂·HOx. A heterogeneous system resulted since the solubility (at 25°) of the adduct in dichloroethane is 2.1 mg/ml. The mixture was maintained at 25° and stirred continuously. At the end of the reaction period, it was quickly filtered (~20 sec) and washed with five 2-ml portions of dichloroethane to remove contaminating [¹⁴C]-HOx. The solid was then converted thermally into UO₂(Ox)₂ and sublimed HOx,³⁴ and the specific activity of each component was determined as described previously.¹¹ The reaction times ranged from 5 min to 3 hr. The 3-hr experiment was repeated with 33 mg (0.047 mmole) of the adduct; all other conditions were unchanged.

Potentiometric titrations

All measurements were made in 50% v/v dioxan-water at 25° and $\mu = 0.10$ (sodium perchlorate). The ligand protonation constants (Table II) were determined potentiometrically and calculated by a least-squares fit of the linear equation previously given.³⁴ Chelate formation constants were determined as described elsewhere.³⁶ In the solution to be titrated (110 ml), the concentrations of ligand and uranium(VI) were 2.2-3.4 × 10⁻³ M and 4.5 × 10⁻⁴ M, respectively. For converting pH-meter readings into -log [H⁺], the correction factor -0.08 was used;³⁵ p_oK_w was 15.37. The general equations of Hearon and Gilbert were used to calculate \bar{n} and [L] values.³⁴ Examination of the formation curves for the 2-Me and 2-n-BuOxH-U(VI) systems led to the selection of data points within the narrow ranges $\bar{n} = 0.3-0.7$ and 0.3-0.6, respectively. Asymmetry in the formation curves above $\bar{n} \sim 0.7$ coincided with observed precipitation in the titrations. For titrations involving the 2-phenyl and 2-(2'-thienyl) substituted ligands, values of $\bar{n} > 0.2$ could not be obtained, because of precipitation of hydrolysed species. After selection of the primary titration data corresponding to the above \bar{n} ranges quoted, the formation constants were calculated (Table II) with the aid of a CDC6400 computer using the programme SCOGS,³⁷ which was modified slightly to suit the needs of the present work.

Derivative	Log K _{NH}	Log K _{OH}	Range ñ	$Log K_1$	Log K2
HOx	4.12	11.12	0.4-1.5	11.42	9.67
2-MeOxH	4.75	11.60	0.3-0.7	10.28	_
2-n-BuOxH	4.58	11.93	0.3-0.6	10.39	
2-(2'-Th)OxH	1.48*	11.64			_
2 PhOxH	2.36	11.77	—		
7-t-BuOxH	2.50	13·4†	0.4-1.2	13.4	11.6

Table II.—Proton and U(VI) formation constants of 2-substituted oxines in 50% aqueous dioxan, $25^{\circ}C$

* Reference 14.

† Estimated value.

RESULTS AND DISCUSSION

The X-ray studies by Hall, Rae and Waters⁹ have shown that the three oxine molecules in $UO_2(Ox)_2$ ·HOx are co-ordinated to the central uranium(VI) atom. Two ligands are bidentate and one is monodentate, being co-ordinated through the oxygen atom only. The three ligands are approximately coplanar about the nearly linear uranyl ion. In view of the interatomic distances and angles, it was suggested that the monodentate ligand is bound as a zwitterion, and that the zwitterion proton is hydrogen-bonded to the oxygen atom of the neighbouring bidentate ligand. This suggestion was proved correct in a subsequent communication¹⁰ in which the present authors showed that the broad 2650 and weak 2050 cm⁻¹ bands in the infrared

spectrum of the adduct (spectrum A in reference 10) arise from the triatomic system $+N-H\cdots O$. These bands were overlooked in previous investigations but are clearly apparent when an increased amount of the adduct is taken for mull preparation. That the bands are due to a protonic vibration is demonstrated by their absence in the spectrum of the sodium salt (prepared by the procedure of Bullwinkel and Noble⁴), and by the appropriate isotopic frequency shifts in the spectrum of the complex precipitated from D_2O ($v_{\rm H}/v_{\rm D} = 1.29$ and 1.35 for the 2650 and 2050 cm⁻¹ bands, respectively). The following evidence clearly associates these protonic bands with the $+N-H\cdots O$ system: (i) similar bands (but of greater intensity) are observed in the spectra of the hydrochloride salts of HOx and of other derivatives such as 2-MeOxH and 8-methoxyquinoline but are not present in those of the neutral ligands; (ii) the bands are similar in appearance and location to the band structure observed for pyridine hydrochloride and other protonated amines.²⁸⁻³³ The broadness of the 2500 cm^{-1} band in the pyridine hydrochloride spectrum and its displacement from the free +N-H stretching frequency (3200-3400 cm⁻¹) have been shown to be due to the $+N-H\cdots$ Cl hydrogen-bonded system; (iii) a molecular model of the adduct, based on the X-ray structure, reveals that the nitrogen proton makes a direct approach to the oxygen atom of the neighbouring bidentate ligand, to which hydrogen-bonding almost certainly must occur. [A strong hydrogen bond, as suggested by the short N—O distance $(0.271 \text{ mm})^9$ would contribute appreciable additional stability to the monodentate ligand.]

The structure of the sodium salt of the adduct would be of considerable interest. Bullwinkel and Noble⁴ have proposed that in the complex anion all ligands are bidentate, but an attempt to determine the structure was not successful.³⁴

The 2650 and 2050 cm⁻¹ bands are of considerable diagnostic value in the characterization of complexes formed between derivatives of HOx and uranium(VI). For example, these bands are observed* in the spectra of the uranium(VI) complexes formed by 2-Me, 5-Me, 5-Cl, 5-Ac, 5-Ph, 5-NO₂ and 7-PhOxH, showing that these compounds are adducts. Typical examples are provided by spectra A, B and C, Fig. 1. Elemental analysis (Table I) confirmed the compositions. The bands are not observed, however, in the spectra of the complexes derived from 7-Me, 2,7-diMe and 7-t-BuOxH, showing that these compounds do not carry the additional zwitterion ligand. Examples are spectra C and D, Fig. 2. In place of the zwitterion, these compounds contain H_2O , NH_3 or acetone, depending on the conditions of preparation. If the 7-MeOxH complex is precipitated by adjusting the pH with dilute ammonia or sodium hydroxide solution, the composition is $UO_2(7-MeOx)_2$ ·H₂O (Table I); the band at 3350 cm⁻¹ and the broad band centred at \sim 3000 cm⁻¹ in spectrum D, Fig. 2, show the presence of water. (A similar hydrate is obtained with 2,7-diMeOxH; the analytical data for this compound strongly suggest the presence of a small amount of reagent contaminant.) Spectrum E, Fig. 2, was obtained after the hydrate had been heated in vacuo for 3 hr at 210° ; the 3350 cm⁻¹ band is now absent, the intensity at \sim 3000 cm⁻¹ is reduced, and the composition of the residue is UO₂(7-MeOx)₂ (Table I). If the pH is adjusted by urea hydrolysis, the composition is $UO_2(7-MeOx)_2 \cdot NH_2$ (Table I), and N-H bands are observed in the spectrum (D, Fig. in reference 10) at 3450 and 3300 cm^{-1} . Because of the low solubility of the reagent in water, the

^{*} In a few instances, the 2050 cm⁻¹ band is scarcely discernible.



FIG. 1.—Infrared spectra of (A) UO₂(5-ClOx)₂·5-ClOxH, (B) UO₂(5-PhOx)₃·5-PhOxH, (C) UO₂(7-PhOx)₃·7-PhOxH.



FIG. 2.—Infrared spectra of (A) contaminated 7-t-BuOxH complex precipitated from aqueous solution, (B) UO₂(7-t-BuOx)₂, (C) UO₂(7-t-BuOx)₃·OC(CH₃)₂, (D) UO₂(7-MeOx)₂·H₂O precipitated with aqueous ammonia, (E) UO₃(7-MeOx)₂.

7-t-BuOxH complex was precipitated from an aqueous solution of $\sim 40\% \text{ v/v}$ acetone-water. The composition of the complex is $UO_2(7\text{-t-BuOx})_2 \cdot OC(CH_3)_2$ (Table I); the infrared spectrum (C, Fig. 2) clearly shows the stretching frequency of the carbonyl group at $\sim 1690 \text{ cm}^{-1}$. The carbonyl band is not present in spectrum B, Fig. 2, which was obtained after the compound had been thermally converted into $UO_2(7\text{-t-BuOx})_2$ (Table I). The value of the 2650 and 2050 cm⁻¹ bands as diagnostic aids was well exemplified when the 7-t-BuOxH complex was precipitated from a purely aqueous medium. Elemental analysis showed that the composition of the precipitate was essentially 1:3, but since the spectrum (A, Fig. 2) gave no evidence of the +N—H ··· O band system, it was concluded that the result was fortuitous and due to reagent contamination.*

The thermal conversion of $UO_2(Ox)_2 \cdot HOx$ into $UO_2(Ox)_2$ yields a spectrum (C, Fig. in reference 10) in which the $+N-H\cdots O$ bands are absent. Similarly, the bands are not present in the spectra of the products obtained on thermal treatment of the adducts of 2-MeOxH and the 5-substituted oxines. Since elemental analysis of these thermal products was not made, it is only presumed that they are the corresponding 1:2 compounds. In general, these thermal products resemble $UO_2(Ox)_2$ in colour (black).

In the light of the infrared band system of the $+N-H\cdots O$ grouping, it is worth commenting on the compound $[UO_2(Ox)_2]_2$ ·HOx first prepared by Bordner *et al.*³⁵ and later examined by Magee and Gordon^{36.37} and Magee and Woodward.³⁸ It has been suggested³⁸ that this compound is an amorphous polymer with the basic polymeric unit composed of the 1:3 and 1:2 compounds held together by a bond between the nitrogen atom of the monodentate ligand and the uranium atom of the 1:2 compound. In turn, the basic polymeric units are bonded by a proton bridge between the uranyl oxygens of the 1:2 compound in adjacent units. This suggestion is probably not correct since the reported infrared spectrum³⁸ of the compound exhibits the $+N-H\cdots O$ band system. Therefore, in $[UO_2(Ox)_2]_2$ ·HOx, the proton is located on the nitrogen atom, and some form of bonding other than that proposed by Magee and Woodward is required to hold the 1:3 and 1:2 components together in a unit, and to expand the unit polymerically.

The construction of Courtauld molecular models shows that the failure of 7-Me, 2,7-diMe and 7-t-BuOxH to form 1:3 adducts is due to interligand steric repulsions. These repulsions are demonstrated in Fig. 3 for the hypothetical 7-MeOxH adduct. The basic structure reported by Hall *et al.*⁹ for the HOx adduct was used as a model. The crosses (7-Me groups) and short lines (α -hydrogen atoms) have been drawn to scale. The heavy dots represent the centres of the hydrogen atoms. The repulsions occur between (*i*) the hydrogen-bonded proton and the 7-Me group of the neighbouring bidentate ligand, (*ii*) the α -hydrogen of the mono-dentate ligand and the 7-Me group of the neighbouring ligand. As a result of these repulsions, smaller co-ordinating species such as H₂O, NH₃ and acetone replace the monodentate reagent molecule.

The formation of an adduct with 7-PhOxH, although initially surprising, is also explicable on the basis of molecular models. In the ligand, the phenyl group is

^{*} The contamination is not completely eliminated by use of a 40% acetone solution, as is evidenced by the high result for %C and %N and low result for %U in Table I.



FIG. 3.-Steric interactions in hypothetical U(VI) adduct of 7-MeOxH.

twisted out of the plane of the quinoline ring because of steric hindrance between (i) the 6-hydrogen atom (quinoline ring) and the 2'-hydrogen atom (phenyl ring), and (ii) the quinoline oxygen atom and the 6'-hydrogen atom. Because of this effect, three such twisted ligands can be arranged equatorially around the uranyl ion and hydrogen-bond formation allowed, provided small deviations from coplanarity around the uranyl-ion are made. An X-ray structure of this compound is required to verify these interactions and would be of considerable interest.

The models also reveal that although considerable crowding exists in the adduct of 2-MeOxH, it is not quite as severe as in the 7-MeOxH adduct, and adduct formation should occur, as is observed. However, it is obvious from the models that substituents of larger size will prevent adduct formation. Thus, attempts to prepare the adduct with 2-n-Bu, 2-Ph and 2-(2'-Th)-OxH failed. Indeed, these ligands did not yield even the ML_2X compounds, as are normally obtained with the 7-substituted oxines. No well-defined chelates were obtained; the precipitate was largely hydrolysed uranium(VI) and precipitated reagent (even in acetone solution).

The failure to precipitate complexes of the type ML_2X is not due to interligand repulsions but to steric interactions between the 2-substituent and one or more water molecules remaining in the co-ordination plane of the uranyl ion. This effect has been previously described for the complexes of 2-substituted oxines and transition-metal ions and results in reduced values of $\log K_1$.¹⁴ In Table II, even though the $\log K_{\rm NH}$ and $\log K_{\rm OH}$ values for 2-MeOxH and 2-n-BuOxH are larger than the corresponding values for HOx, the $\log K_1$ values are lower by more than one log unit. With 2-(2'-Th)-OxH and 2-PhOxH, the combination of a larger substituent and a greatly reduced $\log K_{\rm NH}$ value results in hydrolysis even during addition of the first ligand molecule. Curve D, Fig. 4, for the 2PhOxH system shows hydrolysis beginning at ~pH 4; at ~pH 5.7, a significant amount of solid hydrolysis products is present. Values of \bar{n} did not exceed 0.1. The behaviour of the 2-(2'Th)-OxH system was similar ($\bar{n} < 0.2$).

With the transition metal-ions, the occurrence of distortion towards a tetrahedral configuration on addition of the first ligand molecule relieves the steric interactions and permits substitution of the second ligand molecule without a serious decrease in stability, such that $\log K_2 > \log K_1$.¹⁴ In the present study, hydrolysis prevented the determination of $\log K_2$ values for the 2-MeOxH and 2-n BuOxH systems (Table II;



FIG. 4.—Titration curves for (A) HClO₄, (B) HClO₄/2-MeOxH/U(VI), (C) HClO₄/ HOx/U(VI), (D) HClO₄/2-PhOxH/U(VI), (E) HClO₄/7-t-BuOxH/U(VI) systems. Dashed lines indicate fading of U(VI)-ligand complex colour owing to hydrolysis, and X denotes precipitation of hydrolysis products.

curve B, Fig. 4). This result likely arises from the fact that the essentially linear uranyl ion is not readily distorted, thus allowing hydroxyl ion to compete successfully for the remaining co-ordination sites.

Indirect evidence of the steric interactions with co-ordinated water is provided by the 7-t-BuOxH system (Table II; curve E, Fig. 4). Because the oxygen donor atom, unlike the nitrogen donor atom, is not heterocyclic, the 7-position is not sterically equivalent to the 2-position and, as suggested by molecular models, interference with co-ordinated water should not occur. This is verified experimentally by the log K_1 and log K_2 values, which are normal in all respects.

Experiments involving exchange of the oxine ligands in $UO_2(Ox)_2$ ·HOx with [¹⁴C]-HOx in dichloroethane showed that the extra reagent molecule is co-ordinated and is not a lattice component. Although, in view of the published X-ray structure,⁹ this information is not new, the experiment was deemed important because of its potential application to oxine adducts of other ions for which no X-ray structures are available. It has been previously demonstrated³⁹ that when $UO_2(Ox)_2$ is placed in contact with a solution of HOx, addition of the extra molecule occurs. When [¹⁴C]-HOx is used in place of HOx, the amount of activity found in the addition product (2·0 mV/sec mg), and in the $UO_2(Ox)_2$ (1·9) and sublimed HOx (2·2) obtained on thermal treatment of the addition product, is very high after only a 5-min reaction period. The activity is much higher than expected for the simple addition of [¹⁴C]-HOx to $UO_2(Ox)_2$. Therefore, it was concluded that an exchange process involving the inactive ligands of the bis compound and [¹⁴C]-HOx in solution occurs concurrently with the addition reaction. In the present work, the experiment was repeated with $UO_2(Ox)_2$ ·HOx in place of $UO_2(Ox)_2$. For reaction times of 30 min or less, no

activity was found in the bis compound and sublimed oxine after thermal conversion of the isolated adduct. After 3 hr, the specific activity was small (~0·1 mV/sec mg). For complete exchange of all three ligands, the specific activity should be 1·4 mV/sec mg. (Since 126 mg of the adduct contain 77 mg of inactive HOx, and 52 mg of [¹⁴C]-HOx were dissolved in the dichloroethane, the specific activity after exchange equilibrium is reached should be $[52\cdot0/(77\cdot3 + 52\cdot0)] \times 3\cdot6 = 1\cdot4$ mV/sec mg.) The small amount of activity found is not consistent with a structure in which the extra reagent molecule is a lattice component for, if this was the structure, the isolated adduct (or its thermal decomposition products) would have been highly radioactive after just a few minutes. This follows because on dissolution, the adduct would dissociate into HOx and UO₂(Ox)₂ and as shown previously,³⁹ the bis compound would undergo exchange and addition, rapidly incorporating [¹⁴C]-HOx in the process. The results provide strong evidence, however, that the adduct is dissolved as a molecular entity.

Since solubility equilibrium is achieved in about 5 min, the 3-hr reaction time would appear to be more than adequate for participation in the solubility equilibrium of the total amount of adduct taken. As a precaution, however, the experiment was repeated with 33 rather than 126 mg of adduct. After 3 hr, the specific activity of the isolated adduct and its thermal decomposition products was 0.36 mV/sec mg (2.6 for exchange equilibrium), in accord with the first result.

The main limitation of the test in its application to other adducts is that it probably would not distinguish between a very weakly co-ordinated molecule and a lattice-held molecule.

Acknowledgements—We wish to thank the National Research Council of Canada for support of this research. One of us (M. T.) is grateful to the International Nickel Company of Canada for a much appreciated INCO Fellowship.

Zusammenfassung—Von dem Wasserstoffbrückensystem ^+N —H...O herrührende Infrarotbanden wurden im Oxinaddukt von Uran(VI) identifiziert; sie finden sich auch in den Spektren mehrerer neu hergestellter U(VI)-Addukte von Oxinderivaten. Sterische Effekte zwischen den Liganden verhindern bei den Komplexen der meisten 7-substituierten Oxine die Bildung des 1:3-Adduktes. Statt dessen bilden sich Komplexe von Typ ML₂X, wo X eine in der Lösung vorhandene kleine koordinierende Spezies bedeutet. Bei 2-sub stituierten Oxinen führen sterische Wechselwirkungen zwischen dem 2-Substituenten und dem koordinierten Wasser zu einer Destabilisierung des Komplexes und anschließender Hydrolyse, wenn der pH der Lösung erhöht wird. Experimente mit [¹⁴C]-Oxin unterscheiden zwischen koordiniertem und im Gitter gebundenem Oxin und können bei Untersuchungen von Oxinaddukten anderer Metallionen gegebenenfalls nützlich sein.

Résumé—On a identifié des bandes infra-rouges dues au système ^+N —H...O à liaison hydrogène dans le complexe de l'oxine avec U(VI) et l'on a trouvé qu'elles apparaissent dans les spectres de plusieurs complexes nouvellement préparés de U(VI) avec des dérivés de l'oxine. Les influences stériques interligand dans les complexes de U(VI) avec la plupart des oxines 7-substituées empêchent la formation du complexe 1:3. Les complexes du type ML₂X, où X est une petite espèce coordinante présente en solution, sont formés à la place. Avec des oxines 2-substituées, les interactions stériques entre le substituant en 2 et l'eau de coordination ont pour résultat une déstabilisation du complexe et une hydrolyse subséquente quand on élève

le pH de la solution. On a trouvé que des expériences mettant en jeu l'emploi d'oxine (14C) distinguent entre l'oxine coordonnée et celle fixée par le réseau et sont potentiellement interessantes dans des études sur les composés d'addition que forme l'oxine avec d'autres ions métalliques.

REFERENCES

- 1. R. G. W. Hollingshead, Oxine and its Derivatives, Vol. II, Chap. 28; Vol. IV, Chap. 28, Butterworths, London, 1954.
- 2. T. Moeller and M. V. Ramaniah, J. Am. Chem. Soc., 1954, 76, 5251.
- 3. J. H. Van Tassel and W. W. Wendlandt, ibid., 1959, 81, 813.
- 4. E. P. Bullwinkel and P. Noble, Jr., ibid., 1958, 80, 2955.
- 5. W. E. Clifford, E. P. Bullwinkel, L. A. McClaine and P. Noble, Jr., ibid., 1958, 80, 2959.
- 6. J. H. Van Tassel, W. W. Wendlandt and E. Sturm, ibid., 1961, 83, 810.
- 7. J. E. Tackett and D. T. Sawyer, Inorg. Chem., 1964, 3, 692.
- B. C. Baker and D. T. Sawyer, *ibid.*, 1969, 8, 1160.
 D. Hall, A. D. Rae and T. W. Waters, *Acta Cryst.*, 1967, 22, 258
- 10. A. Corsini and J. Abraham, Chem. Commun., 1967, 1101.
- 11. Idem, Can. J. Chem., 1969, 47, 1435.
- 12. H. Kaneko and K. Ueno, Bull. Chem. Soc. Japan, 1966, 39, 1910.
- 13. H. Irving, E. J. Butler and M. F. Ring, J. Chem. Soc. 1949, 1489.
- 14. A. Corsini and E. J. Billo, Can. J. Chem. 1969, 47, 4655.
- 15. R. G. W. Hollingshead, Anal. Chim. Acta, 1955, 12, 201.
- 16. N. N. Vorozhtsov and A. T. Troshchenko, J. Gen. Chem., USSR, 1938, 8, 431.
- 17. K. Matsumura, J. Am. Chem. Soc., 1930, 52, 4433.
- 18. A. Albert and D. Magrath, Biochem. J., 1947, 41, 534.
- 19. V. Petrow and B. Sturgeon, J. Chem. Soc., 1954, 570.
- 20. R. Long and K. Schofield, ibid., 1953, 2350.
- 21. J. C. Dearden and W. F. Forbes, Can. J. Chem., 1960, 58, 1837.
- 22. T. Moeller and D. H. Wilkins, Inorg. Synth., 1953, 4, 101.
- 23. J. P. Phillips, J. F. Emery and H. P. Price, Anal. Chem., 1952, 24, 1033.
- 24. A. Corsini and J. Abraham, Talanta, 1968, 15, 562.
- 25. A. Corsini and E. J. Billo, J. Inorg. Nucl. Chem., 1970, 32, 1241.
- 26. Idem, ibid., 1970, 32, 1248.
- 27. I. G. Sayce, Talanta, 1968, 15, 1397.
- 28. R. C. Lord and R. E. Merrifield, J. Chem. Phys., 1953, 21, 166.
- 29. R. F. Evans and W. Kynaston, J. Chem. Soc., 1962, 1005.
- 30. R. H. Nuttal, D. W. A. Sharp and T. C. Waddington, ibid., 1960, 4965.
- 31. B. Chenon and C. Sandorfy, Can. J. Chem., 1958, 36, 1181.
- 32. D. Cook, ibid., 1961, 39, 2009.
- 33. G. A. Neville and Z. R. Regnier, ibid., 1969, 47, 4229.
- 34. V. Amirthalingham, Acta Cryst., 1960, 13, 61.
- 35. J. Bordner, E. D. Salesin and L. Gordon, Talanta, 1961, 8, 579.
- 36. R. J. Magee and L. Gordon, ibid., 1965, 12, 441.
- 37. Idem, ibid., 1965, 12, 445.
- 38. R. J. Magee and I. Woodward, ibid., 1966, 13, 709.
- 39. A. Corsini and J. Abraham, Can. J. Chem., 1970, 48, 2360.