Relative Stability Constants of the Uranyl Tropolonate System with Neutral Ligands in Benzene

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The relative formation constants K_L^* of some uranyl tropolonate adducts with neutral ligands L (L = cyclopentanone, pyridine, dimethyl sulphoxide, 4-chloropyridine *N*-oxide, 4-methylpyridine *N*-oxide, triphenylphosphine oxide, and triphenylarsine oxide) of general formula $[UO_2(trop)_2L]$ (Htrop = tropolone) have been determined spectrophotometrically by studying the equilibria $[\{UO_2(trop)_2\}_2] + 2L \rightleftharpoons 2[UO_2(trop)_2L]$ in benzene at 25 °C. The K_L^* sequence obtained can be used as a quantitative scale of donor ability of the various neutral ligands toward the common substrate. Other attempted qualitative correlations based on i.r., ^{1}H n.m.r., and thermal measurements are compared and discussed.

RECENTLY there have been several attempts to determine, at least qualitatively, donor-ability sequences of neutral ligands towards uranyl complexes.[1-10] Several investigations were based on i.r. spectroscopy where attempts were made to interpret $\nu_{asym}(O-U-O)$ shifts on complex formation and/or the differences in frequencies of free and complexed neutral ligands in terms of the donor ability of these ligands.[2,4,11] Critical examination of such data indicates that any suggested relation, even if it leads to apparently acceptable results, has some intrinsic defects because the i.r. stretching frequencies are very close to each other,[2] or, in some cases, because of band splittings due to molecular symmetry or solid-state effects, which reduce the precision of the estimation of the small variations between them and often cause some inversions of sequence when passing from one system to another.[8]

Discrepancies have also been found in attempts to correlate i.r. frequencies and ^{1}H n.m.r. data with some substituent parameters of the neutral ligands,[7] so that no relation was found to exist. Furthermore, it was recently reported[10] for a series of dioxo(pyridine-2,6-dicarboxylato)uranate(VI) adducts with neutral ligands that neither the order of the temperatures at which the monomeric species begin to decompose, chosen as a measure of the thermal stability, nor the order of the i.r. frequencies $\nu_{asym}(O-U-O)$ can be applied as criteria for evaluating the co-ordinating ability of the neutral ligands. Also, the activation energies for thermal loss of neutral ligands, which ought in principle to be a measure of the uranyl–ligand bond-breaking energies, are barely effective because of the simultaneous structural rearrangements which often accompany the release of the neutral ligands.[10]

A direct evaluation of the donor ability of various neutral ligands towards a common substrate, which does not suffer from the above limitations, giving at the same time a quantitative correlation, can be obtained through equilibrium measurements. In this context and in connection with a recent study on the nature of the

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dioxobis(tropolonato)uranium(VI) system, $[\{UO_2(trop)_2\}_2]$ [tropolone (Htrop) = 2-hydroxycyclohepta-2,4,6-trien-1-one], and its monomeric adducts with neutral ligands,[12] we decided to investigate quantitatively the donor ability of some of the common neutral ligands by spectrophotometrically studying the equilibria (1) in benzene at 25 °C (L = cyclopentanone,

$$[\{UO_2(trop)_2\}_2] + 2L \rightleftharpoons 2[UO_2(trop)_2L] \quad (1)$$

pyridine, dimethyl sulphoxide, 4-chloropyridine *N*-oxide, 4-methylpyridine *N*-oxide, triphenylphosphine oxide, and triphenylarsine oxide).

EXPERIMENTAL

Materials.—Reagent-grade uranyl nitrate hexahydrate was used without further purification. Commercial dimethyl sulphoxide, pyridine, cyclopentanone, and benzene were carefully purified and dried before use. 4-Chloropyridine *N*-oxide, 4-methylpyridine *N*-oxide, and triphenylphosphine oxide were prepared as described in the literature.[13,14] Triphenylarsine oxide was obtained from Fluka AG. Tropolone (Aldrich Chemicals) was recrystallized several times from isopentane (m.p. 48—50 °C).

Instruments.—I.r. spectra (400—4 000 cm^{-1}) were recorded on a Perkin-Elmer 577 spectrophotometer with samples mounted as mulls in Nujol between KBr pellets. Calibration of the frequency reading was made with polystyrene films. Electronic spectra of the solutions at equilibrium were recorded on a thermostatted (25 ± 0.05 °C) Optica CF4R double-beam recording spectrophotometer using 1-cm quartz cells.

Preparation of the Complexes.—Bis[dioxobis(tropolonato)uranium(VI)], $[\{UO_2(trop)_2\}_2]$, was prepared as previously reported [12] and its purity was checked by microanalysis and i.r. spectrum. The probable dimeric structure of this complex in the solid state has been discussed in detail.[12] The new monomeric complexes $[UO_2(trop)_2L]$ (L = triphenylarsine oxide, 4-chloropyridine *N*-oxide, and 4-methylpyridine *N*-oxide) were prepared by treating $[\{UO_2(trop)_2\}_2]$ with concentrated solutions of the ligands in benzene. The solids obtained on concentrating the resulting solutions were rapidly washed with benzene and then dried *in vacuo*. The adduct with cyclopentanone was obtained by suspending $[\{UO_2(trop)_2\}_2]$ in the liquid ligand and then removing the excess of ligand *in vacuo* after several hours of stirring at room temperature. Analytical results are reported in Table 1. Uranium was determined gravimetrically as the tetraphenylarsonium salt of dioxo(pyridine-2,6-dicarboxylato)uranate(VI).[15]

Equilibrium Measurements.—Samples of $[\{UO_2(trop)_2\}_2]$ (*ca*. 50 mg) were suspended in rigorously dried benzene (100 cm^3) containing known concentrations of the appropriate ligand L. The mixtures were thermostatted at 25 °C until equilibrium was reached. Conditions were chosen to ensure that there was always some solid present at equilibrium and in each case this solid was found (by i.r. measurements) to be unchanged $[\{UO_2(trop)_2\}_2]$. The electronic spectra (320—520 nm) of the filtered solutions were recorded at the same temperature in the thermostatted compartment of the spectrophotometer. The uranium concentration in the equilibrium solutions was determined by evaporating the solvent, dissolving the residue in a known volume of dimethyl sulphoxide (dmso), and determining the absorption of the $[UO_2(trop)_2(dmso)]$ thus formed for which the molar absorption at 401 nm (wavelength at which all the calculations were made) was carefully determined (ε 7 980 $dm^3\ mol^{-1}\ cm^{-1}$). This procedure, repeated several times on a sample under the same experimental conditions, gave reproducible results to better than 3% and was quantitatively more satisfactory than a direct spectrophotometric determination of $[UO_2(trop)_2L]$ because equilibrium (1) does not allow a direct determination of the molar absorption coefficients of these species in benzene. All the operations were made in a dry-box under anhydrous conditions in order to obtain reproducible results.

TABLE 1

Analytical data (%) for the complexes

		U	C	H	N
$[\{UO_2(trop)_2\}_2]$	Found	46.5	32.8	2.0	
	Calc.	46.5	32.8	1.95	
$[UO_2(trop)_2(cyp)]$	Found	39.95	38.35	2.35	
	Calc.	40.2	38.5	2.35	
$[UO_2(trop)_2(4Cl\text{-}pyo)]$	Found	37.15	35.4	2.25	2.15
	Calc.	37.1	35.55	2.35	2.20
$[UO_2(trop)_2(4Me\text{-}pyo)]$	Found	38.4	38.45	2.7	2.25
	Calc.	38.3	38.65	2.75	2.25
$[UO_2(trop)_2(AsPh_3O)]$	Found	28.7	46.1	3.0	
	Calc.	28.55	46.05	3.0	

cyp = Cyclopentanone and pyo = pyridine *N*-oxide.

RESULTS AND DISCUSSION

In every case the optical density of the solution was a linear function of the ligand concentration; furthermore, addition of an excess of L to solutions that had been separated from the solid did not change the absorption spectrum, which excludes the presence of species such as $[\{UO_2(trop)_2L\}_n]$ ($n \neq 1$). The equilibrium constants are therefore given by $K_L = [UO_2(trop)_2L]/[\{UO_2(trop)_2\}_2]^{\frac{1}{2}}[L]$, where, in the presence of the solid, $[\{UO_2(trop)_2\}_2]^{\frac{1}{2}}$ is constant. The measured optical densities at equilibrium are actually due only to the $[UO_2(trop)_2L]$ species; the solubility of $[\{UO_2(trop)_2\}_2]$ in benzene must be very small as it is spectrophotometrically undetectable. Furthermore addition of an excess of dmso to a saturated solution of $[\{UO_2(trop)_2\}_2]$ in benzene separated from the solid, which allows $[\{UO_2(trop)_2\}_2]$ to be transformed into $[UO_2(trop)_2(dmso)]$ (ε 28 900 $dm^3\ mol^{-1}\ cm^{-1}$ at 337 nm), did not result in a measurable absorption.

A typical plot of $[UO_2(trop)_2L]_{eq}$ against $[L]_{eq}$ is shown in the Figure (L = dmso), where $[UO_2(trop)_2L]_{eq}$ is assumed, under our experimental conditions, to be equal to $[U]_T$ and $[L]_{eq}$ is obtained from equation (2).

$$[L]_{eq} = [L]_{in} - [UO_2(trop)_2L]_{eq} \quad (2)$$

The gradient of the straight line obtained represents the

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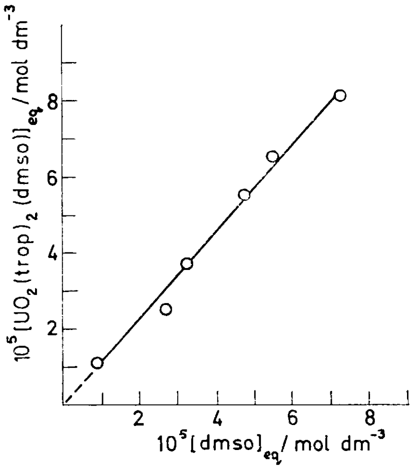
relative constant K_{dmso} $[\{UO_2(trop)_2\}_2]^{\frac{1}{2}}$, indicated as K_{dmso}* for the complex $[UO_2(trop)_2(dmso)]$. All the other ligands gave similar diagrams, the intercepts of the straight lines being zero within the limits of experimental error,† confirming the very low concentration of species other than $[UO_2(trop)_2L]$. It should be noted that, in the case of the reactions with the strongly co-ordinating ligand $AsPh_3O$, it was not possible to obtain values for K* because complex formation goes virtually to completion and it is not possible to use the spectrophotometric method to obtain the concentration of unco-ordinated L, which is less than the experimental error of the method. Experimental K_L* values for L = cyclopentanone, pyridine, dmso, 4-chloropyridine *N*-oxide, 4-methylpyridine *N*-oxide, and PPh_3O are listed in Table 2. The K_L* sequence obtained can be used as a quantitative scale of donor ability of the various neutral ligands towards the common substrate and represents, to our knowledge, the first quantitative correlation. It should be pointed out that the antisymmetric stretching frequencies of the uranyl ion in these complexes (Table 3) are very similar and do not necessarily vary according to the strength of the complex formed with L. They are not therefore useful parameters for the correlation of the donor ability of the various neutral ligands. Discrepancies of the same order were observed in a series of Schiff-base uranyl complexes with neutral ligands,[1] for which the qualitative order of decreasing donor ability PPh_3O > dmso > pyridine > aniline > EtOH, on the basis of spectrophotometric measurements, does not parallel the shift sequence of $\nu_{asym}(O-U-O)$ induced by co-ordination.



Plot of $[UO_2(trop)_2(dmso)]_{eq}$ against $[dmso]_{eq}$ for the reaction $[\{UO_2(trop)_2\}_2]$ + 2dmso $\rightleftharpoons$ $2[UO_2(trop)_2(dmso)]$ in benzene at 25 °C

As far as the i.r. spectral variations of free and complexed ligands are concerned, it is not meaningful to correlate the stretching sequence obtained owing to the non-homogeneity of the ligands. However, in view of the considerable interest in both the parent pyridine *N*-oxide and its many 4-substituted derivatives, we decided to study the interaction of 4-chloropyridine *N*-oxide with the $[\{UO_2(trop)_2\}_2]$ system, in order to compare the results with those obtained for 4-methylpyridine *N*-oxide. In several reports on trends in the nitrogen–oxygen stretching frequency for a number of

TABLE 2

Values of the starting concentrations ($[L]_{in}$) of the various neutral ligands, equilibrium concentrations ($[UO_2(trop)_2L]_{eq}$) of the adducts, relative formation constants for each measurement (K_{L_i}*) and mean K_L* for the equilibria $[\{UO_2(trop)_2\}_2]$ + 2L $\rightleftharpoons$ $2[UO_2(trop)_2L]$ in benzene at 25 °C

L	$[L]_{in}$/ mol dm^{-3}	$10^5[UO_2(trop)_2L]_{eq}$/ mol dm^{-3}	$10^4K_{L_i}$*	K_L*
Cyclopentanone	0.49	4.51	0.92	(0.94 ± 0.06) × 10^{-4} †
	0.55	5.14	0.93	
	0.77	8.14	1.06	
	0.99	8.89	0.90	
	1.47	13.41	0.91	
	1.66	15.29	0.92	
	$10^3[L]_{in}$/ mol dm^{-3}	$10^4[UO(trop)_2L]_{eq}$/ mol dm^{-3}	$10^2K_{L_i}$*	K_L*
Pyridine	1.90	0.43	2.3	(2.2 ± 0.11) × 10^{-2} †
	2.97	0.65	2.2	
	3.60	0.76	2.2	
	5.25	1.14	2.2	
	6.35	1.24	2.0	
	8.88	1.93	2.2	
	$10^5[L]_{in}$/ mol dm^{-3}	$10^5[UO_2(trop)_2L]_{eq}$/ mol dm^{-3}	K_{L_i}*	K_L*
dmso	2.00	1.14	1.32	1.1_5 ± 0.12 †
	5.19	2.51	0.94	
	6.97	3.76	1.17	
	10.23	5.51	1.17	
	12.00	6.52	1.19	
	15.41	8.15	1.12	
4Cl-pyo	3.28	2.63	4.0	4.1 ± 0.20 †
	5.34	4.33	4.3	
	7.37	5.92	4.1	
	8.72	7.01	4.1	
	11.43	9.18	4.1	
	13.30	10.67	4.0	
4Me-pyO	9.28	8.14	7.1	7.0_5 ± 0.35 †
	11.50	10.10	7.2	
	14.58	12.74	6.9	
	16.70	14.66	7.2	
	19.10	16.68	6.9	
	25.32	22.17	7.0	
PPh_3O	4.92	4.58	13.5	16.1 ± 2.5 †
	5.95	5.64	18.2	
	7.52	6.97	12.7	
	8.45	7.97	16.6	
	9.89	9.34	17.0	
	11.34	10.77	18.9	

† Errors are expressed as the standard deviation $\sigma = [\Sigma_m(x_m - x_0)^2/m)]^{\frac{1}{2}}$ when L = cyp, dmso and PPh_3O, and as the instrumental error (±5%) when L = py, 4Cl-pyo, 4Me-pyo because σ is less than the instrumental error.

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† The values of K_L* are therefore given by the mean value of K_{L_i}*.

metal ions, including uranyl ion,[7-9,11,16-21] a correlation was proposed between ν(NO) and Δν(NO) with σ_{pyo} substituent constants,[22] resulting in an increase of both ν(NO) and Δν(NO) with σ_{pyo}. In the present case, on the contrary, comparison of the data (Table 3) for the 4-methyl- and 4-chloro-pyridine *N*-oxide species shows that neither ν(NO) nor Δν(NO) parallel the increase of the two σ values from −0.240 to 0.206, whereas the K_L* values obtained, 7.05 and 4.1 respectively, are in agreement with the decreasing basicity of the ligands. It is to be noted that even in this case, as previously pointed out, ν_{asym}(O–U–O) values (Table 3) cannot be related to the donor ability of the ligands, as indicated by the K_L* values.

TABLE 3

Some characteristic infrared absorptions (cm⁻¹) for the [$UO_2(trop)_2L$] adducts in KBr pellets

L	cyp	py *	dmso *	PPh_3O *	$AsPh_3O$	4Cl-pyo	4Me-pyo
ν_{asym}(O–U–O)	910	904	896	899	882	888	907
Characteristic i.r. absorptions of co-ordinated L		1 605 ν(C=C)	1 018 ν(S–O)	1 152 ν(P–O)	890 ν(As–O)	1 227 ν(N–O)	1 228 ν(N–O)

N–O Stretching frequencies for the neat 4Cl-pyo and 4Me-pyo are at 1 248 and 1 232 cm⁻¹ respectively.

* From ref. 12 and related Supplementary Publication No. SUP 21001.

We now intend to extend this research to homologous series of ligands (aromatic amine *N*-oxides, pyridines, sulphoxides, *etc.*) with the aim of determining the influence of steric, steric–electronic hindrance, and basicity factors on the co-ordinating ability toward the common substrate [{$UO_2(trop)_2$}$_2$]. The study will be also extended to analogous systems containing different uranyl substrates.

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