

SPECTRAL STUDIES ON SOME ORGANIC COMPLEXES OF URANYL ION

Part I. Absorption Spectra of Pyridine Complexes.

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ABSTRACT

The absorption spectra of new crystalline uranyl complexes with pyridine, at 80° K are described. Pyridine uranyl chloride crystallises in two forms, both forms give sharp line like bands at low temperatures. In Form I the bands are analysed in terms of five electronic transitions F, M, D, U and SU of which the former four were suggested for uranyl ion by Dieke *et al.* Results on analogous compounds with deuteropyridine are also reported. Chloride complex seems to have pyridine in the first co-ordination sphere while the acetate complex is of the type of double salt.

INTRODUCTION

INVESTIGATIONS on the spectroscopic properties of uranyl ion under the action of various ligands already exist in literature.¹⁻⁴ A simple organic complexing agent is, however, the pyridine molecule. The effect of this molecule in the sphere of solvation or co-ordination of uranyl ion was found rather interesting and was pursued in some detail. New crystalline uranyl compounds were obtained by the complexing of pyridine with various uranyl salts. Some analogous compounds with deuteropyridine* were also studied. We describe in this paper the absorption spectra of some uranyl complexes with pyridine.

EXPERIMENTAL

Absorption spectra of solutions were obtained on the Hilger Uvispec Spectrophotometer. The spectra of crystalline compounds were photographed on a Bausch and Lomb 1.5 meter grating spectrograph, having

* Kindly sent by Prof. M. Kasha, Department of Chemistry, Florida State University.

a dispersion of 16 Å per mm. The chemicals used were A.R. grade. Purification of pyridine was done by conventional methods.

Pyridine complex with uranyl chloride was found to crystallise in two forms. We call the microcrystalline precipitate obtained on adding pyridine to the solution of uranyl chloride in concentrated HCl as form I which re-dissolves in excess of pyridine and also crystallises as hexagonal plates. Also if the Form I crystals are left in the mother liquor itself for a couple of days at temperatures below 5° C. crystals of Form II having a different morphology begin to grow, those of Form I dissolving as Form II crystals appear. On heating to about 25° C. or above crystals of Form II are converted to Form I. Both Form I and Form II are highly fluorescent and give very sharp bands at low temperatures. With uranyl nitrate and acetate also new crystalline compounds were obtained. The details in the absorption of nitrate complex, however, could not be studied.

(a) Absorption Spectra in Pyridine Solutions

Unlike aqueous solutions, the absorption curves of solutions in pyridine for various uranyl salts consist of broad unresolved bands except for uranyl chloride. In this case eight bands were observed at 4950 Å, 4800 Å, 4640 Å, 4465 Å, 4322 Å, 4195 Å, 4075 Å and 3955 Å respectively. The first band is red shifted with respect to the corresponding band in aqueous solutions.

(b) Absorption Spectra of Crystalline Pyridine Complexes

(i) *Chloride*.—The spectra, at 80° K, for Form I and Form II are shown in Figs. 1 and 2. The spectra have been photographed both by taking a single crystal of microcrystalline powder pressed between two quartz plates. Various series, starting from the longer wavelength side, are termed as fluorescence (F), magnetic (M), diffuse (D), ultraviolet (U) and second ultraviolet (SU). The first four electronic transitions in uranyl salts were suggested by Dieke and Duncan.² Starting of a new transition after the U series was first observed by Pande⁹ in this laboratory. Evidence for these vibronic transitions has also been obtained from spectra of uranyl solutions.^{7, 8, 10}

Form I.—On the basis of intensity considerations and vibrational analysis the five electronic transitions are clearly observed in Form I. The positions of observed bands are given in Table I which also contains the positions of prominent bands for the analogous compound with deuterio-pyridine and the vibrational analysis. The spectra for the two compounds are similar, there is no appreciable shift within 2 cm.⁻¹ in the positions of

TABLE I

Absorption bands of pyridine uranyl chloride and deuterio-pyridine uranyl chloride Form I at 80° K.

Nature	Pyridine uranyl chloride		Deuterio-pyridine uranyl chloride		Designation	Interpretation
	Position in cm.^{-1}	$\Delta\nu$	Position in cm.^{-1}	$\Delta\nu$		
w, s	20064	..	20063	..	a_0	Resonance band
w, s	20081	17	20080	17	..	a_0+17
m, s	20154	90	20155	92	L_1	Ligand
w, s	20260	196	20260	197	L_2	Ligand
m, s	20311	247	20312	249	..	$a_0+\nu_2'$
m, b	20395	331	20394	331	}	M_0 Magnetic Series
S, b	20422	358	20416	353		
vw, b	20452	388		
vw, b	20477	413	$M_0'+L_1$
vw, b	20500	436
w, b	20536	472	20538	475
vw, b	20548	484	$a_1+2\nu_2'$
S, b	20660	596	20656	593	M_1	Magnetic series,
w, s	20770	706	20767	704	..	$a_1+\nu_1'$
m, s	20787	723	20782	718	a_1	a_1+17
m, s	20798	734	20794	731	..	$a_0+\nu_0'$
m, s	20860	796	20859	796	..	a_1+L_1
m, s	20962	898	20960	897	..	a_1+L_2
m, s	21014	950	21015	952	..	$a_1+\nu_2'$
m, b	21098	1034	21096	1033	}	M_1' $M_0'+\nu_1'$
S, b	21120	1056	21117	1054		
m, b	21238	1134
S, b	21346	1288	21338	1275	}	M_1 $M_0+\nu_1'$
S, b	21358	1294	21353	..		
m, b	21369	1305	..	1290	}	a_2 $a_0+2\nu_1'$
m, s	21472	1408	21467	1407		
m, s	21488	1424	21484	1421	}	$a_0+2\nu_1'+17$
m, b	21568	1504	21570	1507		
m, b	21578	1514
vw, b	21662	1598
vw, s	21716	1652	$a_2+\nu_2'$
w, b	21793	1729
S, b	21814	1750	21808	1745	}	M_2' $M_0'+2\nu_1'$
m, b	21839	1775	21832	1769		
w, s	21961	1897	21963	1900	..	$a_2+2\nu_1'$
m, b	22030	1966	22024	1961	}	M_2 $M_0+2\nu_1'$
m, b	22048	1984	22045	1962		

TABLE I—Contd.

Nature	Pyridine uranyl Chloride		Deutero-pyridine uranyl chloride		Designation	Interpretation
	Position in cm. ⁻¹	$\Delta\nu$	Position in cm. ⁻¹	$\Delta\nu$		
<i>w, s</i>	22154	2090	} a_3	$a_0+3\nu_1'$
<i>s, s</i>	22168	2104		$a_0+3\nu_1'+14$
<i>m, d</i>	22210	2146
<i>m, d</i>	22232	2168
<i>m, b & d</i>	22253	2189
<i>m, b & d</i>	22266	2202
<i>w, b</i>	22404	2340	22409	2346
<i>m, b</i>	22496	2432	22480	2416	} M_3'	$M_0'+3\nu_1'$
<i>m, b</i>	22524	2460	22519	2456		
<i>m, d</i>	22644	2580	22648	2582		
<i>w, d</i>	22713	2649
<i>S, d</i>	22738	2674	22747	2684	D_0	Diffuse series
<i>S, d</i>	22759	2694
<i>w, d</i>	22784	2720
<i>w, d</i>	22872	2808
<i>w, d</i>	22904	2840
<i>m, d</i>	22939	2875
<i>m, d</i>	22952	2888
<i>m, d</i>	22992	2928
<i>S, d</i>	23015	2951
<i>S, d</i>	23037	2973	23023	2960
<i>m, d</i>	23098	3034	D_0'	Diffuse series
<i>m, d</i>	23119	3055	23144	3061
<i>m, d</i>	23157	3093
<i>ms, s</i>	23208	3144	23209	3146	M_4'	$M_0'+4\nu_1'$
<i>w, s</i>	23233	3179
<i>w, d</i>	23306	3242	23299	3236
<i>m, d</i>	23349	3275	23346	3283
<i>m, d</i>	23389	3325
<i>m, d</i>	23416	3352
<i>S, d</i>	23443	3379
<i>vS, d</i>	23464	3399	23460	3397	D_1	$D_0+\nu_1'$
<i>m, d</i>	23491	3427
<i>m, d</i>	23571	3507
<i>m, d</i>	23615	3551
<i>m, d</i>	23663	3599
<i>m, d</i>	23687	3623
<i>S, d</i>	23712	3648
<i>vS, d</i>	23737	3673	23725	3662	D_1'	$D_0'+\nu_1'$
<i>S, b</i>	23819	3155	23824	3761

TABLE I—Contd.

Nature	Pyridine uranyl chloride		Deutero-pyridine uranyl chloride		Designation	Interpretation
	Position in cm.^{-1}	$\Delta\nu$	Position in cm.^{-1}	$\Delta\nu$		
<i>w, b</i>	23912	3858	M_6'	$M_0' + 5\nu_1'$
<i>m, d</i>	23987	3923
<i>m, d</i>	24046	3982	24048	3985
<i>m, d</i>	24094	4030
<i>m, d</i>	24123	4059
<i>S, d</i>	24144	4080
<i>vS, d</i>	24172	4106	24161	4098	D_2	$D_0' + 2\nu_1'$
<i>w, d</i>	24271	4207
<i>w, d</i>	24318	4254
<i>w, d</i>	24333	4269
<i>m, d</i>	24378	4314	24376	4353
<i>S, d</i>	24412	4348
<i>vS, b</i>	24435	4371	24423	4360	D_2'	$D_0' + 2\nu_1'$
<i>m, d</i>	24512	4458	24509	4446
<i>w, d</i>	24539	4475
<i>w, d</i>	24743	4679	24750	4687
<i>S, d</i>	24850	4786	24862	4799	D_3	$D_0 - 3\nu_1'$
<i>S, d</i>	24874	4810
<i>w, d</i>	24959	4895
<i>w, d</i>	24991	4827	24982	4919
<i>m, s</i>	25036	4972	25039	4976	U_0'	Ultraviolet series
<i>w, s</i>	25058	4994
<i>S, b</i>	25106	5042	25103	5040
<i>S, b</i>	25129	5063	25128	5065	D_3'	$D_0' + 3\nu_1'$
<i>w, b</i>	25221	5157	U_0	Ultraviolet series
<i>m, b</i>	25434	5370
<i>S, d</i>	25550	5486	25556	5493	D_4	$D_0 + 4\nu_1'$
<i>w, b</i>	25567	5503
<i>vw, d</i>	25659	5595
<i>vw, d</i>	25684	5620
<i>m, s</i>	25730	5666	25732	5669	U_1'	$U_0' + \nu_1'$
<i>m, s</i>	25751	5685
<i>m, b</i>	25798	5734	25795	5732
<i>w, b</i>	25819	5755	25820	5757	D_4'	$D_0' + 4\nu_1'$
<i>m, s</i>	25964	5898	U_1	$U_0 + \nu_1'$
<i>w, d</i>	26224	6160
<i>w, d</i>	26246	6182
<i>w, s</i>	26363	6299	U_2'	$U_0' + 2\nu_1'$
<i>w, s</i>	26400	6336		
<i>m, d</i>	26487	6423	26480	6417	D_5'	$D_0' + 5\nu_1'$
<i>m, d</i>	26508	6444		

TABLE I—*Contd.*

Nature	Pyridine uranyl chloride		Deutero-pyridine uranyl chloride		Designation	Interpretation
	Position in cm. ⁻¹	$\Delta\nu$	Position in cm. ⁻¹	$\Delta\nu$		
w, s	26681	6617	U ₂	U ₀ +2ν ₁ '
m, b	29937	6873	26940	6877	D ₆	
w, s	27012	6948	U ₃ '	U ₀ ' + 3ν ₁ '
w, s	27059	6995		
w, d	27080	7016	D ₆ '	..
vw, d	27114	7050		
w, s	27168	7104
w, b	27398	7334	U ₃	U ₀ +3ν ₁ '
S, s	27771	7707	SU ₀	Second ultraviolet series
S, s	27816	7752		
m, s	27993	7929	SU ₀ +ν ₂ '
m, s	28039	7975
S, s	28464	8398	SU ₁	SU ₀ +ν ₁ '
S, s	28509	8443

sharp bands and the uranyl frequencies are not changed. There is a doublet in the first group of fluorescence series, *i.e.*, a_0 at ca 20063 cm.⁻¹ ($\Delta\nu = 17$ cm.⁻¹). The three uranyl vibrations associated with this series ν_1' , ν_2' and ν_3' are 704 cm.⁻¹, 245 cm.⁻¹ and 732 cm.⁻¹ respectively and the series can be traced to its third member. The ν_1' which alone can be identified with certainty in other series has an approximate value of 700 cm.⁻¹. The M, D and U series have two components each with ca 265 cm.⁻¹, 280 cm.⁻¹ and 180 cm.⁻¹ respectively. Finally, there is observed a series of strong and sharp bands, with a doublet structure ($\Delta\nu = 45$ cm.⁻¹) starting at about 7707 cm.⁻¹ above a_1 . Only two members are observed with a frequency interval of ca 696 cm.⁻¹ and after this the absorption reaches a high value resulting in a continuous absorption. This series is designated as SU (second ultraviolet series). A complete microphotometer tracing of the absorption spectrum is given in Fig. 1 to demonstrate the presence of this series.

Form II.—The observed bands for Form II are given in Table II both for pyridine and deutero-pyridine compounds. Both spectra are similar, however, the crystal for the case of deutero-pyridine happened to be of

TABLE II

Absorption bands of pyridine uranyl chloride and deuterio-pyridine uranyl chloride Form II at 80°K.

Nature	Pyridine uranyl chloride		Deuterio-pyridine uranyl chloride		Designation	Interpretation
	Position in cm. ⁻¹	$\Delta\nu$	Position in cm. ⁻¹	$\Delta\nu$		
w, s	20027	..	20026	..	b_0	Resonance band
vw, s	20041	17	20043	17
vw, d	20156	130	L_1	..
w, d	20270	243	20269	243	..	$b_1 + \nu_1'$
w, d	20284	256	20284	258	..	$b_1 + \nu_1' + 15$
w, b	20338	310	20332	306	L_2	..
w, d	20389	362	20391	365	L_3	Ligands
w, d	20456	429	20453	427	L_4	..
w, b	20479	453	L_5	..
w, s	20564	538	L_6	..
S, b	20598	571	20603	577	M_0	Magnetic series
w, s	20615	589		
w, s	20734	707	20733	707	..	$b_0 + \nu_1'$
w, s	20748	721	20748	722	b_1	$b_0 + \nu_1' + 15$
w, s	20763	736	20764	737	..	$b_0 + \nu_3'$
vw, d	20863	837	..	$b_1 + L_1$
w, d	20977	950	20978	952	..	$b_1 + \nu_2'$
w, d	20989	963	20992	966	..	$b_1 + \nu_2' + 14$
w, d	21039	1012	21041	1015	..	$b_1 + L_2$
w, d	21096	1069	21096	1070	..	$b_1 + L_3$
w, d	21163	1136	21140	1114
w, d	21180	1154	..	$b_1 + L_5$
w, d	21242	1216
vw, s	21268	1242	..	$b_1 + L_6$
S, b	21301	1274	21309	1273	M_1'	$M_0 + \nu_1'$
w, s	21321	1295
w, d	21330	1304
w, s	21429	1404	21428	1403	..	$b_0 + 2\nu_1'$
S, s	21445	1418	21445	1419	b_2	$b_0 + 2\nu_1' + 17$
S, s	21460	1433	21661	1435	..	$b_1 + \nu_3'$
w, b	21499	1472	21488	1462	M_0'	Magnetic series
w, b	21503	1477
w, d	21526	1500
vw, d	21564	1538	..	$b_2 + L_1$
vw, d	21607	1581
w, d	21601	1655	..	$b_2 - \nu_2'$
w, d	21687	1660	21695	1669	..	$b_2 + \nu_2' + 14$
vw, d	21744	1717	21741	1715	..	$b_1 + L_2$
vw, d	21791	1764	21795	1769	..	$b_2 + L_3$
w, d	21859	..	21873	1747	..	$b_2 + L_5$

TABLE II—Contd.

Nature	Pyridine uranyl chloride		Deutero-pyridine uranyl chloride		Designation	Interpretation
	Position in cm. ⁻¹	$\Delta\nu$	Position in cm. ⁻¹	$\Delta\nu$		
<i>vw, s</i>	21960	1960	..	$b_2 + L_6$
<i>S, b</i>	21997	1997	22010	1984	M_2	$M_0 + 2\nu_1'$
<i>vw, s</i>	22019	1993
<i>w, b</i>	22049	2023
<i>vw, s</i>	22117	2090	22106	2080	}	b_3 $b_0 + 3\nu_1'$
<i>w, d</i>	22136	2110		
<i>w, d</i>	22144	2117	22149	2123		
<i>w, d</i>	22185	2159	M_1'	$M_0' + \nu_1'$
<i>w, d</i>	22192	2165	22196	2170
<i>w, d</i>	22244	2218	22247	2221
<i>w, b</i>	22265	2238	..	$b_3 + L_1$
<i>vw, d</i>	22339	2312	..	$b_3 + \nu_2'$
<i>w, d</i>	22425	2398	..	$b_3 + L_2$
<i>w, d</i>	22483	2456	..	$b_3 + L_3$
<i>S, b & d</i>	22581	2554	22583	2556	D_0	Diffuse series
<i>m, d</i>	22699	2672	22696	2669
<i>m, b</i>	22715	2688	22723	2696
<i>m, b</i>	22734	2707
<i>m, d</i>	22787	2760	22788	2761
<i>m, d</i>	22816	2789	22821	2794
<i>m, d</i>	22841	2814	22846	2819
<i>S, b</i>	22879	2852	22876	2849	M_2'	$M_0' + 2\nu_1'$
Red edge	22888	2861
<i>S, vb & d</i>	22925	2898	22911	2884
Violet edge	22977	2950	D_0'	Diffuse series
<i>m, b</i>	23076	3049	23081	3050
<i>m, b</i>	23150	3123	23142	3115
<i>m, b</i>	23192	3165	23197	3170
<i>vS, b & d</i>	23291	3264	23285	3258	D_1	$D_0 + \nu_1'$
<i>m, b</i>	23304	3277
<i>m, b</i>	23338	3311
<i>w, d</i>	23392	3365	23392	3366
<i>w, d</i>	23403	3376	23411	3384
<i>w, d</i>	23455	3428
<i>w, d</i>	23487	3460	23472	3445
<i>w, b</i>	23557	3530	M_3'	..
Red edge } <i>vS</i> }	23493	3466
Violet edge } <i>vS, d</i> }	23638	3611	23569	3542	—	—
Red edge } <i>vS</i> }	23611	3584

TABLE II—Contd.

Nature	Pyridine uranyl chloride		Deutero-pyridine uranyl chloride		Designation	Interpretation
	Position in cm. ⁻¹	ΔP	Position in cm. ⁻¹	ΔP		
Violet edge	23691	3664
w, b	23786	3769	23786	3759
w, b	23820	3793	23849	3822
w, b	23858	3831	23865	3838
w, b	23893	3866	23908	3881
w, b	23926	3899
S, b & d	24013	3986	24001	3974	D ₂	D ₀ +2ν ₁ '
	24051	4024
w, d	24190	4163	24194	4167
w, b	24220	4193	24228	4201	M ₄ '	M ₀ '-4ν ₁ '
red edge	24309	4282
vS, b & d	24337	4310	D ₂ '	D ₀ '+2ν ₁ '
violet edge	24391	4364
w, d	24600	4573	24612	4585
s, b	24698	4671	24704	4677	D ₃	D ₀ +3ν ₁ '
s, b	24966	4939	24984	4957
w, d	25016	4989	25005	4978
s, b	25037	5010	25052	5025	D ₃ '	D ₀ +3ν ₁ '
S, b	25061	5034	25075	5048
m, b	25392	5365	25404	5377	D ₄	..
vw, b	25596	5569	25596	5569	}	U ₀ Ultraviolet series
vw, b	25639	5612	25625	5598		
vw, d	25670	5643	25688	5661	M ₆ '	M ₀ '+6ν ₁ '
w, b	25720	5693	25730	5703
S, b	25733	5706	25750	5723	D ₄ '	D ₀ '+4ν ₁ '
m, b	25751	5724	25770	5743
vw, s	26163	6136	26167	6140	}	U ₀ Ultraviolet series
vw, s	26189	6162	26178	6151		
m, b	26285	6258	26255	6228	}	U ₁ ' U ₀ +ν ₁ '
w, s	26298	6271	26305	6278		
S, b	26425	6398	26448	6421	D ₁ '	..
w, s	26880	6853	26885	6858	}	U ₁ ..
w, s	26903	6876	26901	6874		
S, b	27010	6983	27025	6998	U ₂ '	..
w, b	27136	7109	27126	7099	D ₆	..
u, b	27712	7685	27695	7668
m, d	27806	7779	27833	7806	D ₇ '	..
S, d	27900	7873
S, d	27936	7909	27965	7938
Heavy absorption	28281	..	28300

a suitable thickness for greater details of absorption to be investigated. A number of vibrations, other than uranyl frequencies, were thus found associated with the fluorescence series. The spectrum is classified in four series. The absorption beyond U series could not be studied because thin single crystal could not be obtained of an adequate size. On making a thin film with powder the crystalline modification was found to get converted partly to Form I, thus making the spectrum very complicated.

(ii) *Acetate*.—The spectrum is shown in Fig. 3 and the observed bands are given in Table III with assignments. The fluorescence series starts with b_0 at *ca* 20974 cm^{-1} . A series of strong bands, M series, starts at *ca* 773 cm^{-1} above b_0 and can be followed upto its fourth member with repetition frequency of *ca* 690 cm^{-1} and consists of doublets with $\Delta\nu = 300$ cm^{-1} . The doublet nature of D series, which starts at about 1660 cm^{-1} above b_0 , is evident after its second member ($\Delta\nu = 355$ cm^{-1}). The frequency interval between successive members of this series is about 715 cm^{-1} . A series of comparatively sharper bands starts at about 6040 cm^{-1} above fluorescence series and is designated as U series in conformity with the general usage. From *ca* 7990 cm^{-1} above b_0 the absorption seems to become continuous.

DISCUSSION

The identification of various electronic transitions in the pyridine complexes has been made through vibrational analysis, structure of bands and intensity considerations. In the case of diffuse bands with multiplet structure the vibrational analysis becomes unreliable, however, the second criterion is helpful that the intensity in the second group is higher than the first group and falls again after the second or the third group. It is an experimental generalisation that in almost all cases M, D and U series are doublets with separations varying from 150 cm^{-1} to 400 cm^{-1} , the violet member being in general weaker. In uranyl sulphate a doublet separation of this order has also been observed in fluorescence series.^{5,6,11} It is again a general observation that in going from a single salt to a double salt M series becomes more intense than D or F series. The solutions also accord with this conclusion where anionic complexing enhances M series and with hydrolysis D series becomes intense. In solid hydrolysed samples also M series is known to get weaker than in normal salt. The spectrum of pyridine uranyl acetate resembles that of double acetates, the M series bands are rather broad and have highest intensity. Pyridine complexes with uranyl

TABLE III

Absorption bands of pyridine uranyl acetate at liquid air temperature

Nature	Position in cm.^{-1}	$\Delta\nu$	Designation	Interpretation
<i>w, s</i>	20974	..	b_0	Resonance band
<i>vw, d</i>	21104	130
<i>w, b</i>	21149	175
<i>w, b</i>	21209	235	..	$b_0 + \nu_2'$
<i>w, b</i>	21237	263	L	Ligand
<i>w, b</i>	21665	691
<i>S, b</i>	21704	730	b_1	$b_0 + \nu_3'$
<i>VS, vb</i>	21747	773	} M_0	Magnetic series
<i>VS, vb</i>	21831	857		
<i>vw, b</i>	21922	948
<i>vw, b</i>	21983	1009
<i>S, b & d</i>	22049	1075	M_0'	Magnetic series
<i>vw, b</i>	22341	1367
<i>vw, b</i>	22384	1310	b_2	$b_0 + \nu_1'$
<i>VS, vb</i>	22423	1459	} M_1	$M_0 + \nu_1'$
<i>VS, vb</i>	22551	1577		
<i>S, vd</i>	22635	1661	D_0	Diffuse series
<i>S, b & d</i>	22749	1775	M_1'	$M_0' + \nu_1'$
<i>Vw, b</i>	22821	1847
<i>vS, vb</i>	23108	2134	} M_2	$M_0 + 2\nu_1'$
<i>vS, vb</i>	23246	2272		
<i>S, d</i>	23305	2331	} D_1	$D_0 + \nu_1'$
<i>S, d</i>	23350	2376		
<i>S, b & d</i>	23457	2501	M_2'	$M_0' + 2\nu_1'$
<i>S, b & d</i>	23704	2730	} D_1'	Diffuse series
<i>S, d</i>	23793	2819		
<i>VS, vb</i>	23840	2866	} M_3	$M_0 + 3\nu_1'$
<i>VS, vb</i>	23959	2985		
<i>S, d</i>	24018	3044	} D_2	$D_1' + \nu_1'$
<i>S, vb & d</i>	24160	3186		
<i>S, vb & d</i>	24404	3430	} D_2'	$D_2' + \nu_1'$
<i>S, vb & d</i>	24586	3612		
<i>S, b & d</i>	25085	4111	D_3'	$D_1' + 2\nu_1'$
<i>w, b</i>	25564	4590
<i>vw, b</i>	25817	4843	D_4'	$D_1' + 3\nu_1'$
<i>S, s</i>	27016	6042	U_0	Ultraviolet series
<i>S, d</i>	27666	6692
<i>w, b</i>	27746	6742	\bar{U}_1	$U_0 + \nu_1'$
<i>w, b</i>	27840	6865
<i>S, vb & d</i>	28478	7504	SU_0	New series starts
Heavy absorption	28969	7995

v—very, *w*—weak, *S*—strong, *m*—moderate, *s*—sharp, *b*—broad and *d*—diffuse.

chloride partly resemble the double chlorides and partly the unhydrolysed single chlorides. The spectra are red shifted with respect to the single salt and violet shifted compared to double salt (caesium uranyl chloride).⁹ The red shift seems to originate due to basic nature of pyridine in the first co-ordination sphere. Red shift is also observed in spectra of pyridine solutions with respect to the corresponding aqueous solutions. The resemblance of spectra, with single salts in that D and M series are almost equally intense and also with the double salts so far as red shift is concerned, indicates both anionic and nitrogen complexing in the equatorial plane of uranyl ion. The intimate structure and positions of various bands are not altered in the analogous compound with deuterio-pyridine. An interesting feature of the spectra of pyridine uranyl chloride complexes is the extra sharpness of bands. The multiplet structure of D series could thus be observed. Each member of D series (red component) is found to consist of four bands, the interval of stronger central components is *ca* 20 cm^{-1} and that of wings on either side *ca* 25 cm^{-1} . The members of D' series consist of three bands each, the separation being 23 cm^{-1} . There have been indications regarding a new transition to start after U series in a number of solids as well as solutions.⁹ In pyridine uranyl chloride Form I this transition is brought forth very clearly. It is not to be confused with U series which is weak. The bands of U series are clearly recognised by their sharp character among the broad bands of diffuse series.

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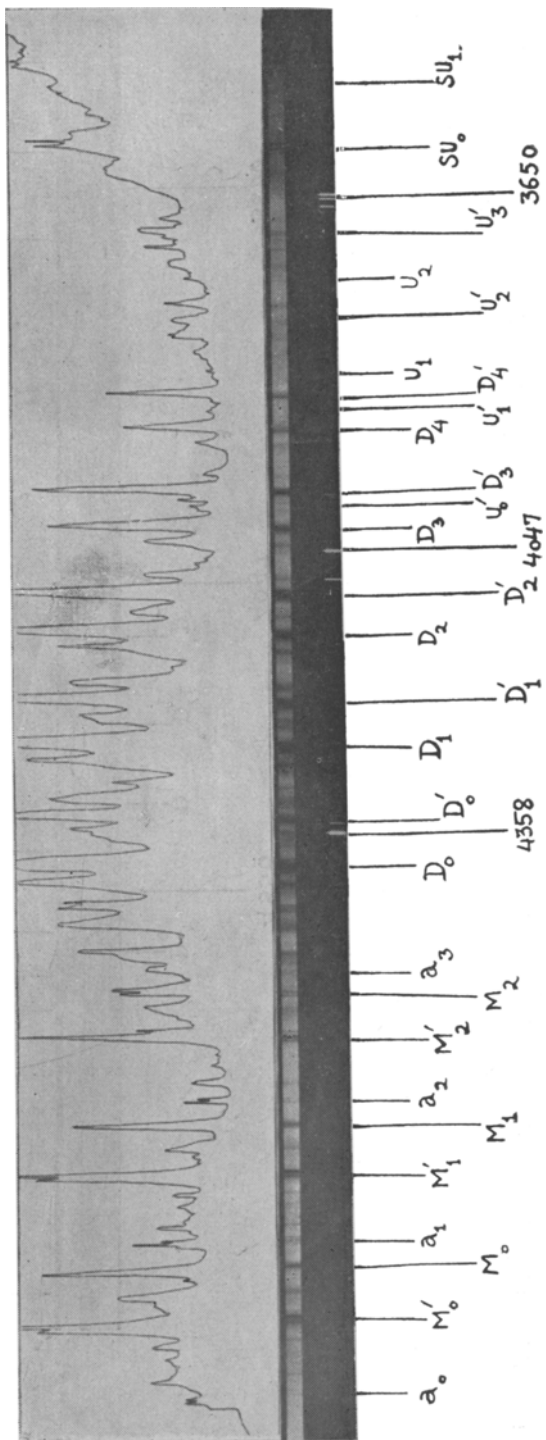


FIG. 1. Absorption spectrum of pyridine uranyl chloride form I at liquid air temperatures along with complete micro-photometer tracing.

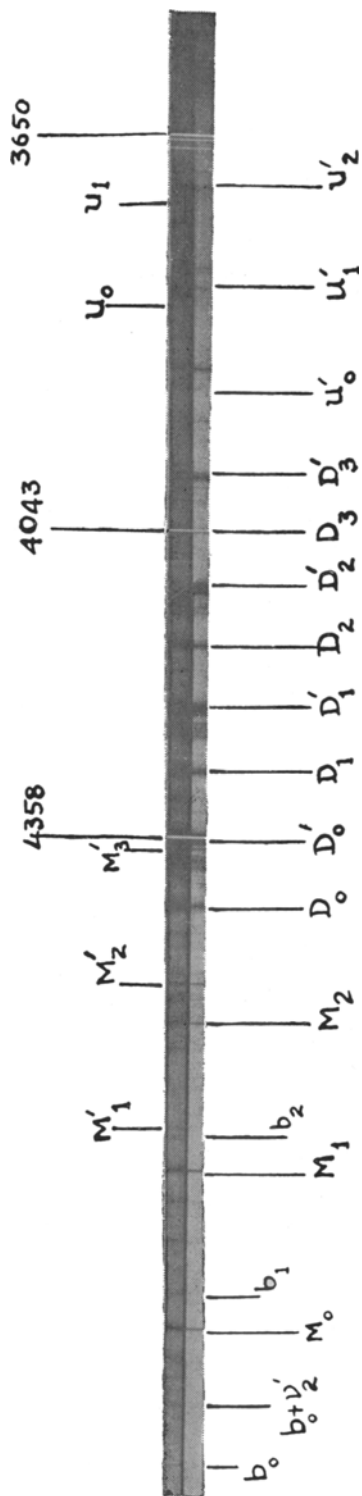


FIG. 2. Absorption spectrum of pyridine uranyl chloride form II at liquid air temperature.

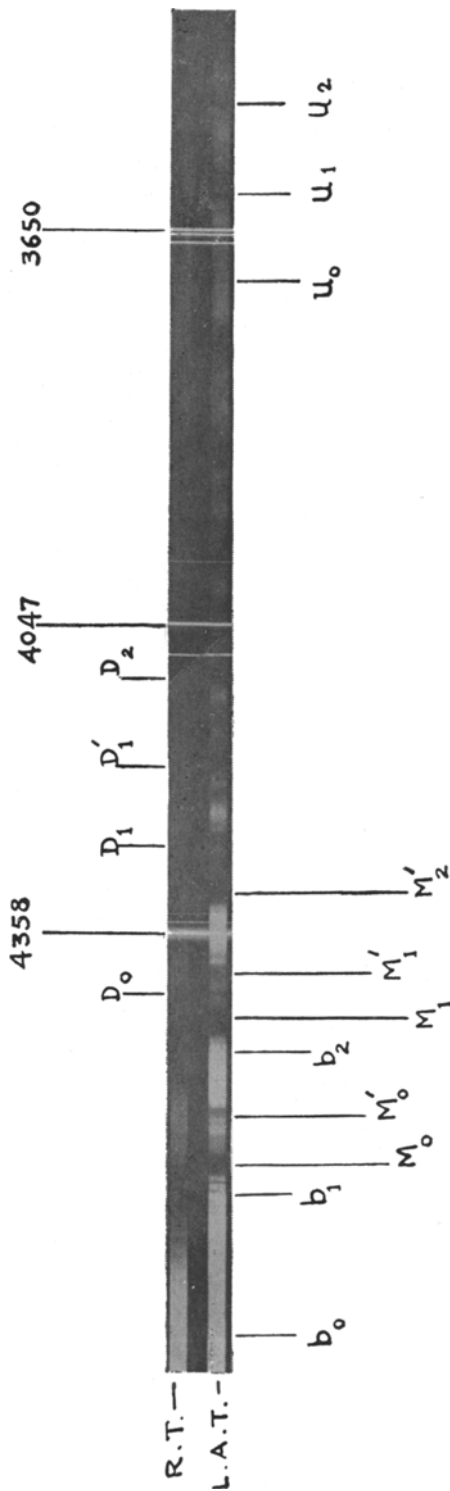


FIG. 3. Absorption spectrum of pyridine uranyl acetate at liquid air temperature and room temperature.