

CHAPTER III

Synthesis and spectroscopic investigation of uranium(VI) complexes of pyrimidine and pyridine Schiff bases and their peroxo derivatives

Two series of uranyl heterocyclic schiff base complexes (1) and (2) of 2-aminopyrimidine salicylaldehydes and 2-aminopyridine salicylaldehydes respectively and their peroxo derivatives (3 and 4) have been synthesized. The complexes have been characterized by elemental analyses, IR and thermogravimetric measurements. The peroxo contents have been determined by iodometric titration and are found to be thermally stable.

1. Introduction :

Pyrimidine bases represent an important class of biologically active molecules¹. Their derivatives found applications as drugs of various activities and uses¹⁻³. Metal complexes of them have received great attention during recent years⁴⁻¹¹. In this chapter, the synthesis characterization and peroxo complexes of uranium(VI) Schiff bases derived from salicylaldehydes and 2-aminopyrimidine will be described. Their 2-aminopyridine analogues are also reinvestigated. The pyridine Schiff base uranyl complexes are reported earlier^{12,13} and the structure elucidation is criticised¹⁴.

2. Results and Discussion :

a. Ligands and Complexes :

The complexes are synthesized by refluxing the mixture of respective salicylaldehydes, 2-aminopyrimidine or 2-aminopyridine and $\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ in 2:2:1 mole ratio as described in experimental part¹². The figures of the complexes are in **Table III.1** and the analytical data are set out in **Table III.2**. The ligands act as monobasic bidentate NO donor system.

B. Physical Characteristics :

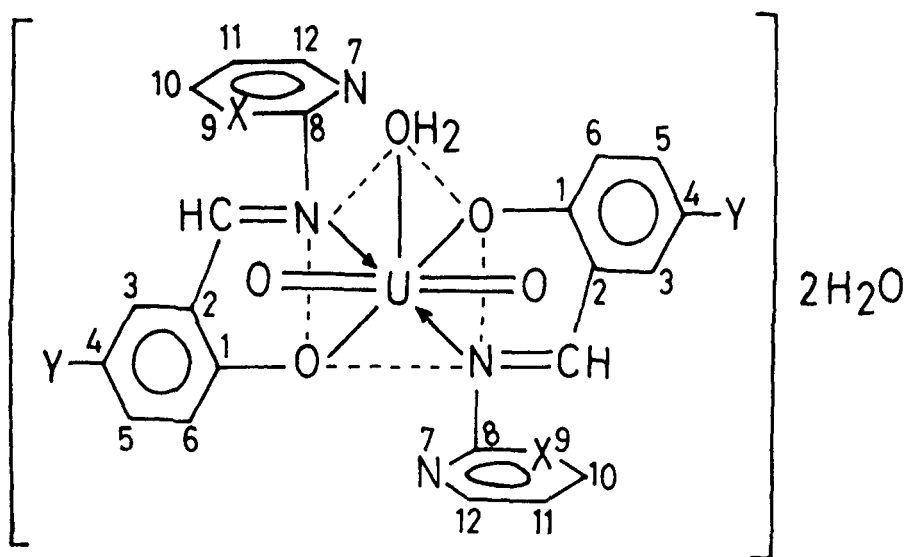
The complexes do not have a sharp m.p. and get decomposed on heating. The complexes are poorly soluble in organic solvent like methanol, chloroform, acetonitrile, benzene etc. The molecular weights of the complexes could not be determined by cryoscopic method or by any other method due to lack of specific arrangements. The molar conductances in DMSO ($\Lambda \Rightarrow 1-3 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) show that complexes are non-electrolytes indicating that the chelate anions are covalently bonded in all the cases. The complexes are diamagnetic as expected for $5f^0$ system.

The peroxo compounds are brown, diamagnetic ($\mu = 0-0.5 \text{ B.M.}$) and ESR silent. In the presence of dilute H_2SO_4 , they dissolve in water and the liberated H_2O_2 is estimated iodometrically¹⁵. The analytical data showed the U(VI):O_2 : heteroligand ratio as 1:1:2 in agreement with the figures (**Table III.1**) and the formulae (**Table III.2**).

C. Spectral Characterisation :**(i). UV-VIS Spectra :**

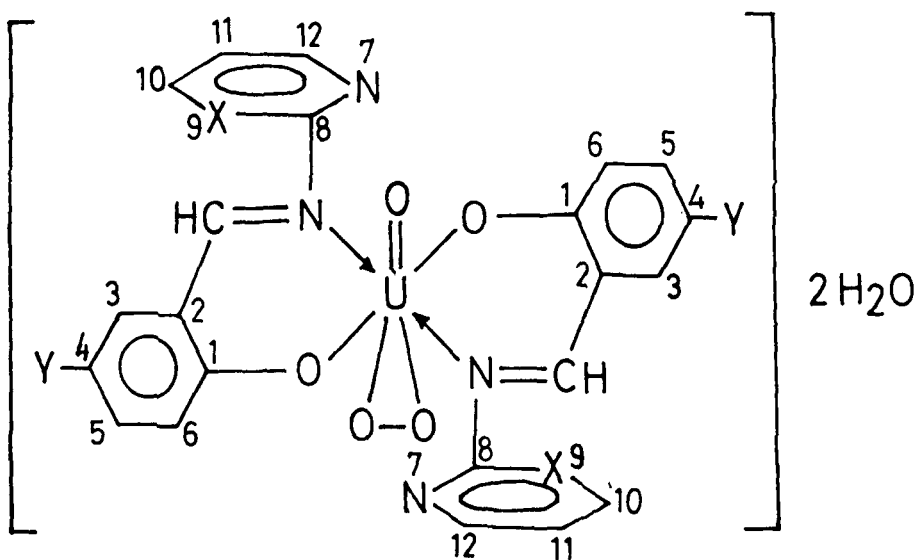
The electronic spectra of the complexes have been recorded in DMSO. Three spectral transitions centred at 260-270, 300-320 and 360-420 nm are observed. The first two transitions may be

Table-III.1



1 and 2

X = N(1), X = CH(2)



3 and 4

X = N(3), X = CH(4)

Y	H	Cl	3,4-Benzo
	<u>a</u>	<u>b</u>	<u>c</u>

Table III.2

Analytical data of uranyl complexes and peroxy derivatives

Compound	M.pt (°C)	Found (Calcd.)%				Peroxo
		C	H	N	U	
$[(C_{11}H_8N_3O)_2(H_2O)UO_2] \cdot 2H_2O$ (1a)	>320	36.52 (36.67)	2.94 (3.06)	11.49 (11.67)	33.19 (33.06)	-
$[(C_{11}H_7N_3ClO)_2(H_2O)UO_2] \cdot 2H_2O$ (1b)	>340	33.58 (33.46)	2.40 (2.53)	10.58 (10.65)	29.92 (30.16)	-
$[(C_{15}H_{10}N_3O)_2(H_2O)UO_2] \cdot 2H_2O$ (1c)	>350	43.81 (43.90)	3.26 (3.17)	10.31 (10.24)	28.89 (29.02)	-
$[(C_{11}H_9N_2O)_2(H_2O)UO_2] \cdot 2H_2O$ (2a)	>290	39.86 (40.11)	3.51 (3.34)	7.92 (7.80)	32.93 (33.15)	-
$[(C_{12}H_8N_2ClO)_2(H_2O)UO_2] \cdot 2H_2O$ (2b)	>300	36.72 (36.59)	2.72 (2.80)	7.26 (7.12)	30.31 (30.24)	-
$[(C_{16}H_{11}N_2O)_2(H_2O)UO_2] \cdot 2H_2O$ (2c)	>320	47.02 (46.94)	3.36 (3.42)	6.94 (6.85)	29.18 (29.09)	-
$[(C_{11}H_8N_3O)_2UO(O_2)] \cdot 2H_2O$ (3a)	>300	36.84 (36.77)	2.62 (2.79)	11.82 (11.70)	33.01 (33.15)	4.28 (4.46)
$[(C_{11}H_7N_3ClO)_2UO(O_2)] \cdot 2H_2O$ (3b)	>310	33.47 (33.55)	2.38 (2.29)	10.52 (10.67)	30.12 (30.24)	3.89 (4.07)
$[(C_{15}H_{10}N_3O)_2UO(O_2)] \cdot 2H_2O$ (3c)	>340	44.11 (44.01)	3.02 (2.93)	10.36 (10.27)	28.92 (29.10)	3.72 (3.91)
$[(C_{11}H_9N_2O)_2UO(O_2)] \cdot 2H_2O$ (4a)	>280	40.18 (40.22)	3.12 (3.07)	7.68 (7.82)	33.10 (33.24)	4.19 (4.47)
$[(C_{12}H_8N_2ClO)_2UO(O_2)] \cdot 2H_2O$ (4b)	>280	36.78 (36.69)	2.46 (2.55)	7.01 (7.13)	30.18 (30.32)	3.82 (4.08)
$[(C_{16}H_{11}N_2O)_2UO(O_2)] \cdot 2H_2O$ (4c)	>300	46.92 (47.06)	3.02 (3.19)	6.97 (6.86)	29.02 (29.17)	3.70 (3.92)

Table III.3

UV-VIS Spectral data

Complex	λ max (in nm)		
<u>1a</u>	260	300	390
<u>1b</u>	265	305	400
<u>1c</u>	265	305	415
<u>2a</u>	260	305	390
<u>2b</u>	260	310	360
<u>2c</u>	270	315	420
<u>3a</u>	270	312	380
<u>3b</u>	270	315	390
<u>3c</u>	270	320	410
<u>4a</u>	265	310	395
<u>4b</u>	265	310	400
<u>4c</u>	265	320	415

ascribed to intraligand charge transfer bands $\Pi \rightarrow \Pi^*$ and $n \rightarrow \Pi^*$ transitions^{16,17} respectively. The third transition may be due to apical oxygen $\rightarrow f^0(U)$ transition¹⁸. The data of electronic spectra are in **Table III.3**.

(ii). *IR spectra* :

In the IR spectra, the absence of band around 3100-3300 cm^{-1} assigns the disappearance of $-\text{NH}_2$ group in pyridine or pyrimidine ring¹⁹ or engaged otherwise. A new band appears centred at 1600-1610 cm^{-1} in uranyl complexes which also remains unaffected in their peroxo derivatives can be assigned to the coordinated $\sqrt{(\text{C}=\text{N})}^{20}$ involving coordination through the nitrogen atom of the azomethine group since the free $\text{C}=\text{N}$ stretch is at 1640 cm^{-1} in the aromatic Schiff base²¹. This accounts the condensation of aldehyde and amine group under the template condition. Note that the ligands have not been prepared at pure state by simple condensation process. The coordination of phenolic $-\text{OH}$ is evidenced from the absence of vibrational band around 3200 cm^{-1} ²². The broad diffuse band centred at 3470 cm^{-1} is observed for all complexes and is assigned to O-H stretching modes for water. The spectra showed a band around 740-760 cm^{-1} that

correspond to rocking mode of coordinated water^{23,24} in agreement with the formulae of complexes (Table III.2). The $\nu(\text{C-O})$ (phenolic) band in complexes appears at 1500 - 1530 cm^{-1} ²⁵. This region is overlapped with ring stretching modes of heterocyclic moiety and hence broadened. Four characteristic ring breathing modes¹⁷ heterocyclic group 1565-1580, 1525-1540, 1435-1450 and 1400-1420 cm^{-1} of in the complexes and are slightly blue shifted on metal chelation. The stretching at $\sim 550 \text{ cm}^{-1}$ and 310 cm^{-1} are assigned to $\nu(\text{U-O})$ (phenolic) and $\nu(\text{U-N})$ respectively. The peroxo derivatives (3 and 4) are characterised by three IR bands due to metal peroxo groupings²⁶⁻²⁸ $\nu(\text{C}_{2v} \text{ symmetry})$: $\nu_1(\text{O-O})$ 800-810 cm^{-1} , the symmetric stretch $\nu_2(\text{U} \begin{array}{c} \diagup \text{O} \\ | \\ \diagdown \text{O} \end{array})$ 580-590 cm^{-1} and the antisymmetric $\nu_3(\text{U} \begin{array}{c} \diagup \text{O} \\ | \\ \diagdown \text{O} \end{array})$ 630-640 cm^{-1} . All the complexes display very strong bands at 910-915 cm^{-1} assignable to $\nu(\text{O=U=O})$ modes^{22,29} in (1) and (2) and $\nu(\text{U=O})$ modes²⁶ in (3) and (4). The force constant ($F_{\text{U=O}}$) for the U=O bond mode have been calculated according to the published procedure³⁰ and the values (7.00-7.45 mdynes/\AA^0) agree well with those of similar uranyl complexes^{22,31}. The $F_{\text{U=O}}$ value in each case was used to calculate the U=O bond length using Jone's formula³⁰ and the present value (1.71-1.73 \AA^0) are in

Table III.4
Some selected infrared spectral data^a
 ν , in cm^{-1}

Complex	$\nu(\text{O-H})$	$\nu(\text{C-N})$	$\nu(\text{C-O})$	$\frac{\nu(\text{O=U=O})}{\nu(\text{O=U})}$	$\nu(\text{U-O})$	$\nu(\text{U-N})$	$\nu_1(\text{O-O})$	$\nu_2(\text{U} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array})$	$\nu_3(\text{U} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array})$
<u>1a</u>	3470	1630	1530	912	555	310	-	-	-
<u>1b</u>	3465	1635	1525	910	550	312	-	-	-
<u>1c</u>	3470	1638	1520	910	545	312	-	-	-
<u>2a</u>	3470	1640	1525	912	540	312	-	-	-
<u>2b</u>	3460	1640	1525	915	540	310	-	-	-
<u>2c</u>	3465	1638	1530	910	540	310	-	-	-
<u>3a</u>	3468	1635	1525	910	545	310	800	580	640
<u>3b</u>	3465	1635	1525	915	550	308	805	585	640
<u>3c</u>	3465	1638	1525	912	550	308	800	585	635
<u>4a</u>	3470	1640	1528	912	550	310	810	590	630
<u>4b</u>	3465	1640	1530	910	545	312	810	590	635
<u>4c</u>	3468	1640	1530	910	540	310	805	585	640

^a In KBr disk

the expected range ($1.60 - 1.92 \text{ \AA}$)²². The representative spectral figures are given in Fig. III.A and some selective data are given in Table III.4.

D. *Thermal Analysis* :

The complexes were subjected to thermal analyses in air under non-isothermal conditions. The complexes (1) and (2) lose weight at 110-130°C corresponding to two water molecules present in lattice while the mass loss at 170-200°C is equivalent one coordinated water molecule. The IR spectra also confirm the presence of coordinated water (*vide supra*). The mass loss at 320-600°C is most significant which corresponds to the remaining organic part and the final residue is U_3O_8 . The thermal analysis of peroxo complexes ((3) and (4)) assigns the presence of two lattice water molecules those eliminate at 80-120°C and active oxygen is released at 210-230°C and finally to U_3O_8 , without giving any intermediate³².

E. *Epilogue* :

The analytical data including spectral and thermal analysis suggest that the Schiff bases formed in the reaction medium are monobasic bidentate ligand. The complexes attain more or less pentagonal bipyramidal geometry by coordinating the H_2O for

remaining coordination position.

3. Experimental :

A. *Materials* :

Salicylaldehyde was a Sarabhai M reagent while 5-chlorosalicylaldehyde, 2-aminopyridine, 2-aminopyrimidine, were Aldrich reagents. 2-Hydroxy-1-naphthaldehyde was obtained from Fluks, $\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ was BDH reagent. H_2O_2 , methanol, chloroform, acetonitrile, DMSO and other solvents were obtained from S.D.'s Lab. Chem. Industry.

B. *Physical Measurements* :

The elemental analyses, electronic spectral studies, IR, magnetic susceptibility measurement and thermal analyses were carried out as in Chapter I. Uranium was estimated gravimetrically as $\text{UO}_2(\text{Oxin})_2$, OxinH and as ignited U_3O_8 ^{15(a)} or uranium was estimated from the residue of thermal analysis as U_3O_8 . The peroxo content was estimated by dissolving the peroxo derivatives in H_2SO_4 and titrating the liberated H_2O_2 by iodometrically^{15(b)}.

C. *Preparation* :

The complexes are of two types : complexes of pyridine and

pyrimidine Schiff bases with salicylaldehyde, 5-chlorosalicylaldehyde and 2-hydroxynaphthaldehyde and the peroxo derivatives of the above Schiff bases complexes.

1. Complexes (1 and 2):

Type 1 complexes (1 and 2) were prepared according to a common procedure.

An ethanolic solution of salicylaldehyde (0.25g, 2.1 mmol) was added to ethanolic solution of 2-aminopyrimidine (0.2g, 2.1 mmol) and the mixture was refluxed on a water bath for 30 min. It was added to an ethanolic solution of $\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.42g, 1.0 mmol) and the contents refluxed for 2 hr. The orange red precipitate appeared, which was filtered, washed with ethanol and dried in vacuo; yield 70%.

2. Peroxoderivatives (3 and 4):

The peroxo derivatives of the Schiff base complexes were synthesised by the literature procedure²⁶.

The ethanolic solution of the salicylaldehyde (0.25g, 2.1 mmol) and 2-aminopyrimidine (0.2g, 2.1 mmol) was refluxed on water bath for 30 min as before and KOH (0.12g, 2.1 mmol) was added to this solution followed by $\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.42 g, 1.0 mmol) in ethanol.

The solution was refluxed for another 30 min and then 30% H_2O_2 (10ml) in excess was added dropwise and refluxing continued for an additional 1 hr. The resulting brown-red precipitate was filtered after cooling and washed successively with ethanol, ether and dried in vacuo; yield 60%.

References :

1. R.M. Acheson; "An Introduction to the Chemistry of Hetrocyclic Compounds", Wiley Eastern Ltd., New Delhi 2nd edn.; 1976,333.
2. A.R. Katritzky; "Advances in Hetrocyclic Chemistry", Academic Press, New York, 1982,32.
3. A.R. Katritzky and C.W. Rees; (eds) "Comprehensive Hetrocyclic Chemistry", Pergamon Press, New York 3, 1984,57.
4. G. Smith, C.H.L. Kennard and K.A.Byriel; *Polyhedron*, 1991,10,873.
5. A.A. Gad; A.A. Gabr and M.A. El-Taher; *Asian J. Chem*, 1991,3,99.
6. I. Yakovidis, G. Varvoumin and N. Madjiliadin; *Inorg. Chim. Acta*, 1988,151,165.
7. M. Goodgame and D.A. Jakubovic; *Coord. Chem Rev.* 1987, 79, 97.
8. R.B. Martin; *Acc. Chem. Res.*, 1985,18,32.
9. B.T. Khan, A. Gaffuri and Safia; *Indian. J. Chem.* 1982, 21A, 630.
10. L.K. Mishra; *J. Indian. Chem. Soc.* 1982,59,408.
11. R.W. Bockman, F.M. Jr. Schabel and J.A. Montgomery; *Biochem Pharmacol*, 1977,26,2193.
12. S.I. Gusev, V.I. Kumov, E.V. Sokolova and A.S. Pesis; *Russ. J. Inorg. Chem.*, 1961,6,958.

13. A. Savich, A.K.Pikaev, V.G. Lebedev, E.V. Kuz'Michwa and V.I. Spitsyn; *Russ. J. Inorg. Chem.*, 1962,7,254.
14. U. Casellato; M.Vidali and P.A. Vigato; *Inorg. Chim. Acta.*, 1976,18,77.
15. A.I. Vogel; "A Text Book of Quantitative Inorganic Analysis", ELBS and Longmans, London, 1962,(a)363 and (b)540.
16. R.M. Silverstein, G.C. Bassler and T.C. Morill; "Spectrometric indentification of organic Compounds", John Wiely & Sons, New York,1981.
17. A.R. Katritzky, (ed); "Physical Methods in Hetrocyclic Chemistry"; Academic Press, New York, 1971, III.
18. R.A. Lal, L.M. Mukherjee, A.N. Siva, A. Pal, S. Adhikari, K.K. Narang and M.K. Singh; *Polyhedron*, 1993, 12,2351.
19. L.K. Mishra; *J. Indian Chem Soc.*, 1982,59,408.
20. K.C. Rout, P.K. Mishra and K.C. Dash; *Indian. J. Chem.*, 1994,33A,673.
21. H.H. Freedman; *J. Am. Chem. Soc.* 1961,83,2900.
22. A. Syamal, D. Kumar and S. Ahmad,*Indian. J. Chem.*, 1982, 21A,634.
23. M.K.Chaudhuri, P. Srinivas and D.T. Khathing; *Polyhedron*,1993,12,227.
24. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and

- Coordination Compounds", Wiley Interscience, London 4th edn., 1986,228.
25. U. Casellato, P. Guerriero, S. Tamburini, S. Sitran and P.A. Vigato; *J. Chem. Soc. Dalton Trans.*, 1991,2145.
 26. M.T.H. Tarafdar and A.A.M. Anwarul Islam; *Polyhedron*, 1989,8,109.
 27. M.T.H. Tarafdar and A.R. Khan; *Polyhedron*, 1991,10,819.
 28. M. Bhattacharjee, M.K. Chaudhuri and R.N. Dutta Purakayastha; *J. Chem. Soc. Dalton Trans.*, 1990,2883.
 29. E.M. Nour, A.M. Al-Kority, S.A. Saddek and S.M. Teleb; *Synth. React. Inorg. Met-org. Chem.*, 1993,23,39.
 30. L.H. Jones, *Spectrochim Acta.*, 1959,15,409.
 31. S.P. McGlynn, J.K. Smith and W.C. Neely; *J. Chem. Phys.*, 1961,35,105.
 32. C. Duval; "Inorganic thermogravimetric analyses"; translated by R.F. Gesper; Elsevier, Amsterdam, 1963.

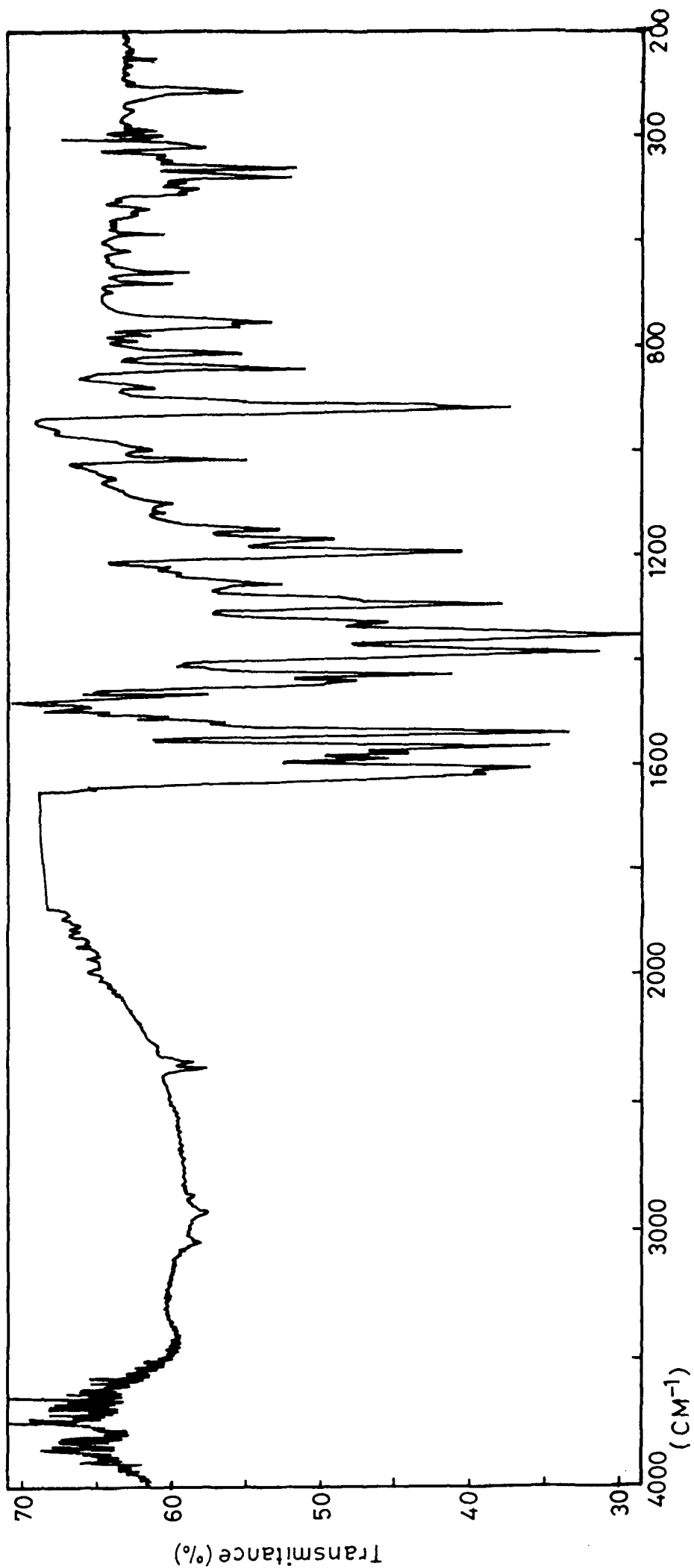


Fig. III.A. (for complex 1c).

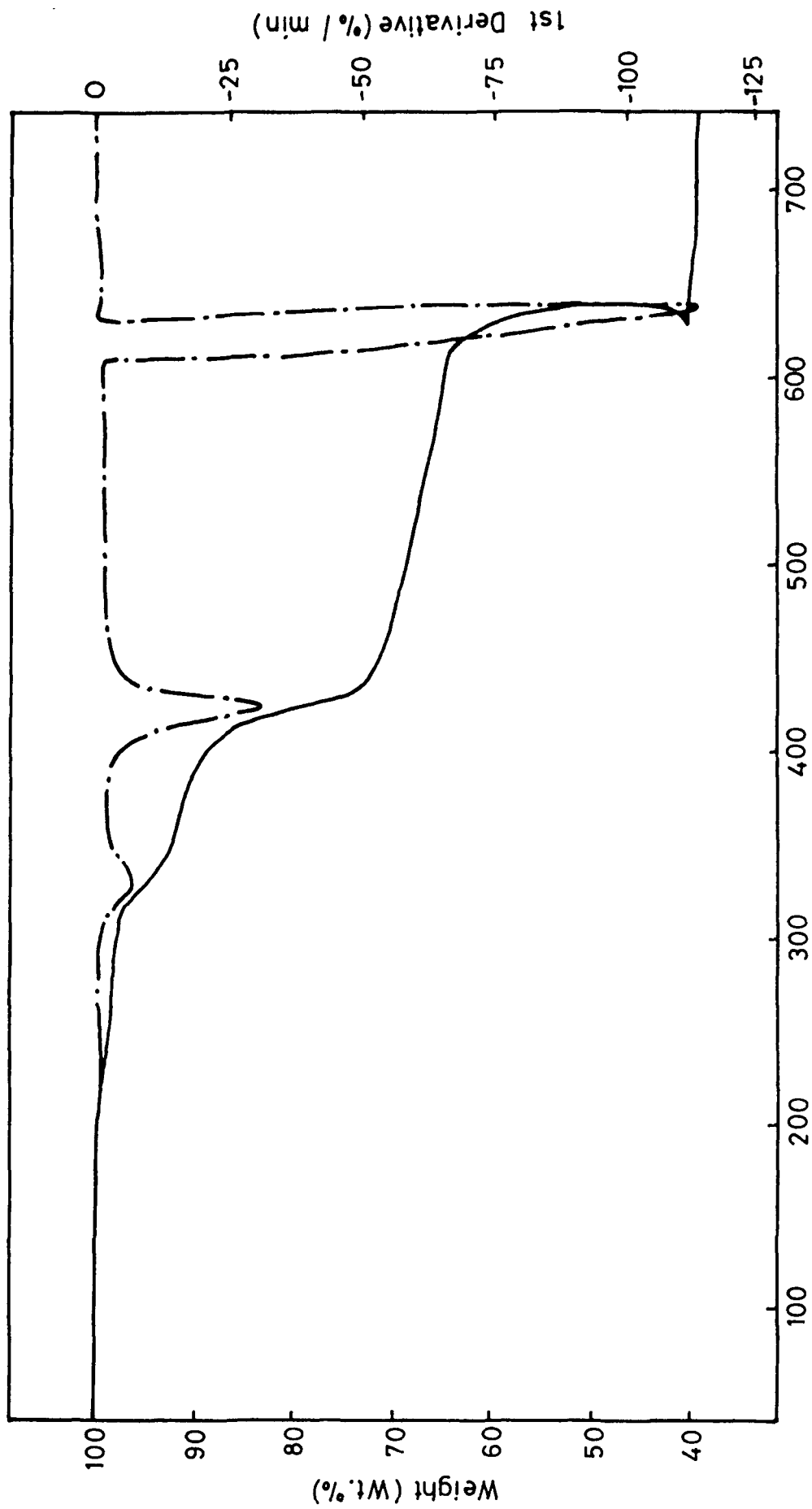


Fig. III.B. (for complex 1c).