

the detector from neutron irradiation were computed and applied to the observed gamma intensities. The 182 keV transition was found to be the strongest one and intensities of the other components were expressed relative to this. These results are summarized in Table I. For a comparison, the results of Giannini *et al.*³, who used a similar experimental method for low energy gamma rays, are also included in the same table. However, the region of interest in ref. (3) confines only to a few transitions. Some of the lines observed in this work and interpreted as multiplets are indicated by 'm' in Table I. The present measurements are in accordance with those due to the other experimental methods⁴.

DISCUSSION

The ground state spin⁵ of the target nucleus ¹⁴¹Pr is 5/2⁺ while that of the product nucleus⁶ is 2⁻. The capture of a *s*-wave neutron will result in the formation of the initial state of ¹⁴²Pr with a spin-parity of either 3⁺ or 2⁺. In this situation, primary gamma rays of pure E1 type are expected to populate the low lying levels due to the decay of the capture state in ¹⁴²₅₉Pr₈₃. The 83rd neutron has a spin-parity 7/2⁻ which in the shell model classification is characterised by the ($\nu f_{7/2}$) configuration. The odd proton (59th) may be expected to occupy the ($\pi d_{3/2}$) configuration. In the shell

model description, one expects a formation of six states from ($\pi d_{5/2}$ / $\nu f_{7/2}$) configuration mixing with spins 1 to 6 and negative parities. From the energy systematics of odd-odd nuclei⁶, the present gamma components with energies 85, 137 and 182 keV may be regarded as those due to the transitions taking place between the corresponding states and the ground state of ¹⁴²Pr. The other components may be ascribed to the transitions taking place in the multiplets formed by configuration mixing of orbitals describing the ground and first excited states.

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NIBIUM(V) COMPLEXES WITH AROMATIC SCHIFF BASES

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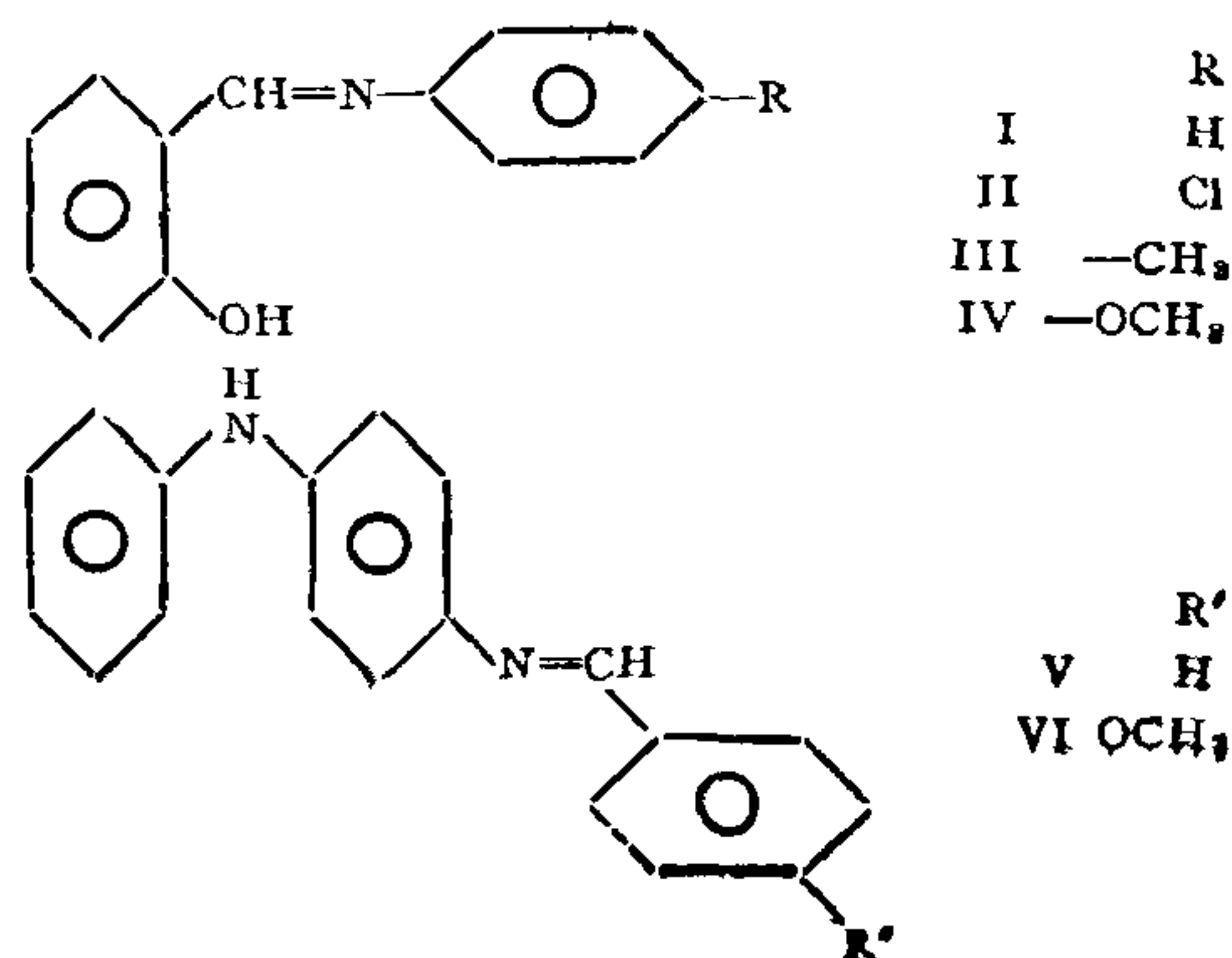
ABSTRACT

Six niobium(V) complexes with aromatic Schiff bases have been prepared in chloroform and characterised by elemental analysis. These are non-electrolytes in DMF. Infrared spectra have been reported and all the complexes are regarded to have coordination a number of seven.

INTRODUCTION

THE complexes of niobium(V) with wide range of Schiff bases containing a variety of donor sites have been reported in the literature¹⁻⁴. They have shown that in almost all the complexes the coordination number of niobium is seven. Prashar and Tandon⁵ have recently reported hexa- and octa-coordinate Schiff base complexes of niobium(V) and tantalum(V).

This report concerns the synthesis and spectral studies of niobium(V) complexes with the following Schiff bases,



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- (i) Salicylidine-aniline.
- (ii) Salicylidine-*p*-chloroaniline.
- (iii) Salicylidene-*p*-toluidine.
- (iv) Salicylidene-*p*-anisidine.
- (v) Benzylidene-*p*-aminodiphenylamine.
- (vi) Anisylidene-*p*-aminodiphenylamine.

EXPERIMENTAL

Niobium(V) chloride was of Fluka grade and the remaining chemicals used for the reactions were of reagent grade. The commercial chloroform was dried over fuming sulphuric acid and distilled before use. The Schiff bases were prepared according to the method reported elsewhere⁶.

Niobium pentachloride (0.01 mole) in chloroform was treated with the Schiff base (0.022 mole) in the same solvent with vigorous shaking, and allowed to stand for several hours. The precipitated complex was filtered, washed with chloroform and dried in vacuum over phosphorus pentoxide.

The dry mass was powdered and extracted with dry ether in a soxhlet apparatus and dried at 50–60°C. All the preparations were carried out in a dry box in the absence of moisture.

ANALYSIS

Niobium in the complexes was determined gravimetrically as Nb₂O₅, chloride as AgCl, and nitrogen by the Kjeldhal method. The analyses are given in Table I.

stoichiometry with niobium(V) chloride. The molar conductance values, in DMF at the concentration 10⁻³ M fall in the range of 1.0–5.0 ohm⁻¹ cm²/mole. These values are too low to account for the behaviour of the complexes as electrolytes; the complexes can therefore be considered as non-electrolytes in DMF.

INFRARED SPECTRA

The important infrared frequencies and their tentative assignments are given in Table II. A strong band found in the region 1620–1590 cm⁻¹, assignable to the C=N stretch⁷ of the bases, is observed in the complexes in the region 1650–1610 cm⁻¹. The observed shift obtained in the C=N stretch after complexation suggests that azomethine nitrogen is coordinated to the metal ion. The broad, weak band in the region 2800–2600 cm⁻¹, assignable to the intramolecular hydrogen bonded –OH⁸ in the bases I–IV, is not found in the complexes. The absence of this band in benzylidene-*p*-aminodiphenyl and anisylidene-*p*-aminodiphenylamine confirms this assignment. The strong band in the region 1280–1250 cm⁻¹ of the bases I–IV, due to the phenolic C–O, is found in the region 1335–1315 cm⁻¹ in the complexes. This is indicative of niobium-oxygen bond formation with oxygen of the *o*-OH group of the bases. The infrared spectrum of bases V and VI show a band around 3300 cm⁻¹ which is attributed to the –NH stretch of the secondary amine group. This band

TABLE I
Elemental analysis of niobium(V) Schiff base complexes

Lig. No.	Compound No.	Empirical formula	% Nb		% Cl		% N		Colour
			Found	Calc.	Found	Calc.	Found	Calc.	
1	2	3	4	5	6	7	8	9	10
I	VII	(C ₁₃ H ₁₀ ON) ₂ NbCl ₃	15.82	15.74	17.98	18.13	4.76	4.75	Yellow
II	VIII	(C ₁₃ H ₉ ONCl) ₂ NbCl ₃	14.15	14.31	16.17	16.21	4.23	4.24	„
III	IX	(C ₁₄ H ₁₂ ON) ₂ NbCl ₃	15.15	14.99	17.13	17.26	4.49	4.51	„
IV	X	(C ₁₄ H ₁₂ O ₂ N) ₂ NbCl ₃	14.51	14.38	16.26	16.42	4.38	4.30	„
V	XI	(C ₁₀ H ₁₆ N ₂) ₂ NbCl ₆	11.61	11.45	20.38	20.58	6.79	6.89	Violet
VI	XII	(C ₂₀ H ₁₈ ON ₂) ₂ NbCl ₆	10.83	10.63	19.96	20.03	6.31	6.41	„

PHYSICOCHEMICAL MEASUREMENTS

The molar conductance was measured with an ELICO conductivity bridge type CM-32, with a cell constant of 0.829 cm⁻¹. The infrared spectra of the ligands and the complexes, in nujol mull, were recorded on a Beckman IR-20 recording spectrometer in the region 4000–600 cm⁻¹.

RESULTS AND DISCUSSION

The analytical data given in Table I show that all the six Schiff bases form complexes of 1:2

does not show any splitting in the complexes XI and XII, indicating that the –NH group has not taken part in the coordinate bond formation (Table II).

All these observations lead to the following conclusions.

1. In all the complexes (VII–XII), the azomethine nitrogen has taken part in the coordinate bond formation. As a result of this the bond order of carbon to nitrogen link is increased.

TABLE II

Infrared frequencies (in cm^{-1}) of Schiff bases, niobium(V) complexes and their assignments

I	VII	II	VIII	III	IX	IV	X	V	XI	VI	XII	Assignments
2994	2950	2959	2950	2985	2930	2985	2930	2905	2950	2910	2950	=CH and aromatic CH stretching
2632	..	2703	..	2632	..	2632	Intramolecular H-bonded OH
1613	1645	1603	1630	1616	1650	1616	1640	1598	1610	1608	1650	C=N stretching
1587	1585	1582	1590	1592	1610	1600	1590	1600	..	1510	..	Aromatic C=C stretching
1567	1525	1563	1530	1567	1550	1564	1550	1575	1550	1480	1550	
1481	1455	1475	1435	1495	..	1488	1450	1497	1490	
1278	1335	1266	1315	1279	1325	1272	1320	Phenolic C—O stretching
..	3340	3330	3300	3280	—NH stretching

2. Disappearance of hydrogen bonded —OH in the³ complexes (VII–X) and high frequency shift of the phenolic C—O stretch are the suggestive of niobium-oxygen bond formation.
3. Non-splitting of —NH stretch in the complexes XI and XII indicates that —NH group of the bases V and VI has not taken part in the complex formation.

STEREOCHEMISTRY

Niobium(V) chloride forms complexes of 1:2 stoichiometry with bases I–IV losing two of the five chlorides whereas it forms 1:2 adducts with bases V and VI (Table I). All these complexes are non-electrolytes in DMF. These observations taken together with spectral observations suggest that niobium(V) has coordination number seven in these complexes.

For coordination number seven, there is no simple arrangement of the ligands such that all the nearest neighbours are at equal distances. Nyholm and coworkers⁹ have given various stereochemical arrangements for coordination number seven. Amongst them, capped trigonal prism (1:4:2 stereochemistry) is supposed to be the most favoured configuration¹⁰. With the existing data the stereochemistry of these complexes is not clear. By analogy with diarsine complexes⁹ and the prevailing majority of "1:4:2" stereochemistry, it seems possible that these complexes may favour "1:4:2" stereochemistry.

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