

TITANIUM(IV) COMPLEXES OF BENZOYL HYDRAZONES

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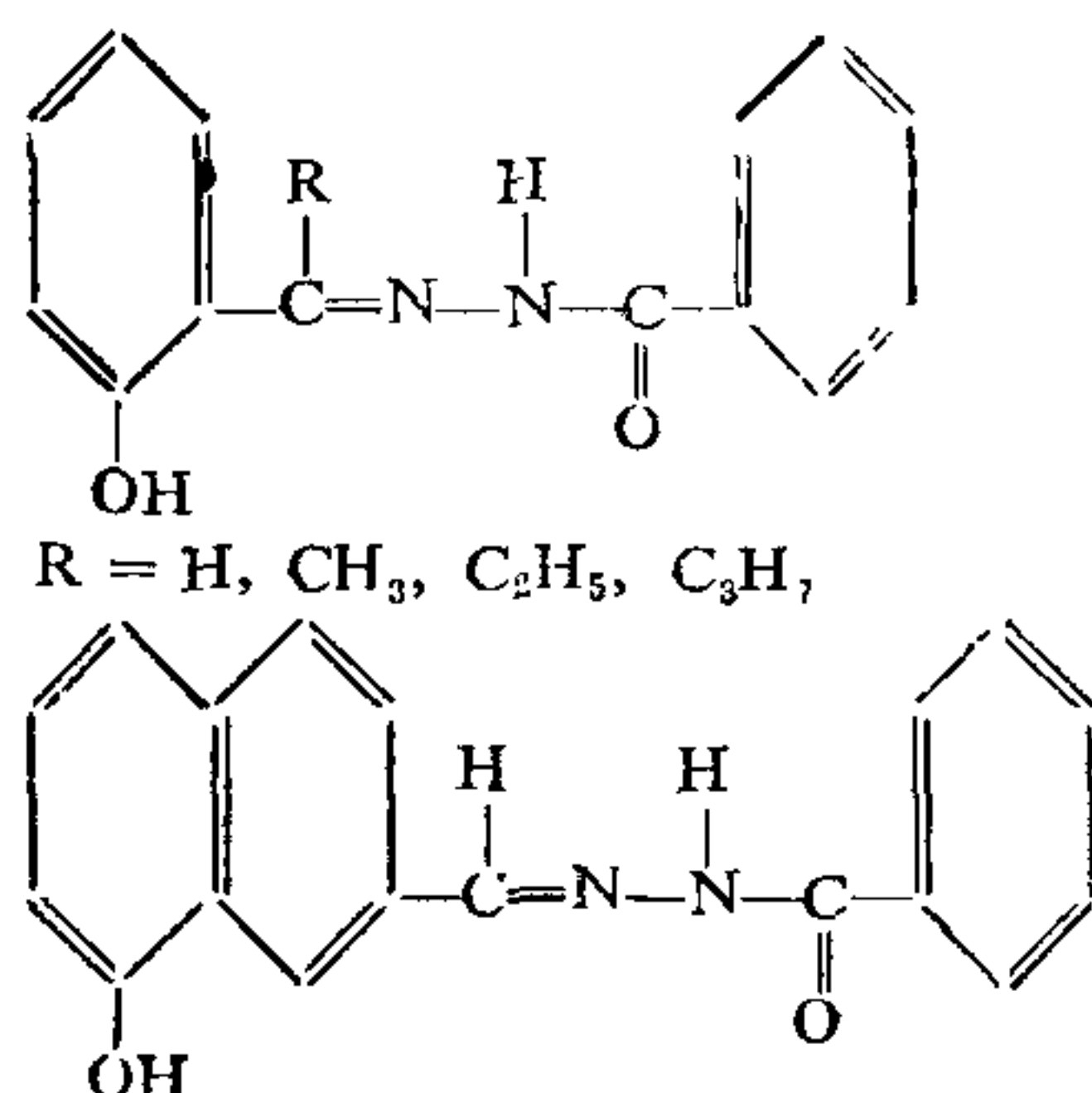
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ABSTRACT

Titanium(IV) complexes of benzoyl hydrazones derived from benzhydrazide and salicylaldehyde (BSH), *o*-hydroxyacetophenone (BAH), *o*-hydroxypropiophenone (BPH), *o*-hydroxybutyrophenone (BBH) and 2-hydroxynaphthaldehyde (BNH) have been described. These complexes have been characterised by elemental analyses, and by conductance, magnetic, infrared and electronic spectral measurements. The complexes have trans-octahedral stereochemistry as indicated by ν (M-N) and ν (M-O) vibrations in far infrared region.

INTRODUCTION

INTEREST in the coordination chemistry of titanium(IV) ion continues to increase on account of its capability to form coordination compounds having unusual coordination numbers¹⁻³. A number of such studies are available with Schiff bases⁴⁻⁸. In this paper, we report the synthesis and characterisation of titanium(IV) compounds with benzoyl hydrazones whose structures are given below :



EXPERIMENTAL

All the reagents used were of Analar grade. The ligands were synthesised by the method of Struve⁹. They all gave satisfactory analyses for C, H, N and their purity was further checked by TLC.

Synthesis of Complexes

The titanium(IV) chloride was (0.001 mole) diluted to 50 ml with absolute alcohol. The addition of 0.002 mole of the ligand in 50 ml acetone to the above solution instantaneously gave a bright red precipitate. It was digested for about 15 minutes at 70° C, cooled, filtered and washed several times with acetone. The product was recrystallised from chloroform and dried in vacuum.

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The conductance, magnetic moment, i.r. and electronic spectral measurements were made as reported previously¹⁰. Titanium was estimated gravimetrically as titanium dioxide. Analytical data are given in Table I.

RESULTS AND DISCUSSION

The analytical data reveal 1 : 2, metal : ligand stoichiometry and the complexes are represented by general formula [Ti(Lig)₂]. They are soluble in acetone, alcohol, chloroform, DMF and DMSO. The molecular conductance measurements in DMF (25° C) indicate that these complexes are non-electrolytes. This formulation is further supported by infrared spectra.

The i.r. spectra of the ligands show a strong band between 3200–3250 cm⁻¹ which may be assigned to ν (OH) vibrations involving hydrogen bonding. The intramolecular hydrogen bonding is also indicated by the presence of weak broad band at 2700–2775 cm⁻¹ in the free ligands^{5,11}. The bands at 3000–3050 cm⁻¹ are assigned to ν (NH).

Strong bands in the region 1660–1675, 1615–1625 and 1600 cm⁻¹ in the free ligand may be assigned to amide I (due to ν C=O), ν (C=N) (azomethine) and phenyl ring vibrations^{5,12}, respectively. The bands around 1515, 1250, 650 and 495 cm⁻¹ may be assigned to amide II (ν CN+ δ NH), amide III (ν CN), amide IV (C=O out of plane deformation) vibrations, and amide VI (C=O in plane deformation, respectively, indicating that the ligands are present in keto form¹²⁻¹⁴.

Dramatic changes are found in the spectra of the complexes which show no band characteristic of amide and amino group suggesting that the ligands are not bound in keto form. The ν (C=N) band shows a downward shift (15–20 cm⁻¹) with slight loss of intensity. This downward shift indicates the coordination of azomethine nitrogen. A new band appearing at \sim 1598 cm⁻¹ seems to have its origin in the stretching vibration mode of the conjugate () C=N – N=C () grouping analogous to that of azine¹⁵, suggesting the participation of enolic oxygen. The disappearance of bands 3200–

TABLE I
Analytical Data

Compound	Colour	Percentage composition							
		C	H	Calcd. N	Ti	C	Foind H	N	Ti
Ti (BSH) ₂	Bright red	63.89	4.21	10.61	9.10	64.12	4.25	10.55	9.02
Ti (BAH) ₂	Light brown	64.98	4.73	10.10	8.64	64.80	4.75	10.01	8.75
Ti (BPH) ₂	Light brown	65.98	5.19	9.62	8.22	65.50	5.22	9.70	8.30
Ti (BBH) ₂	Brown	66.88	5.61	9.17	7.84	67.02	5.55	9.10	7.90
Ti (BNH) ₂	Yellowish red	69.16	4.18	8.94	7.64	69.01	4.10	8.96	7.60

TABLE II
Important infrared bands (in cm⁻¹) and their assignments

Compound	Amide I	ν (C = N)	() C = N – N = C ()	ν (Ti – N)	ν (Ti – O) Phenolic	ν (Ti – O) enolic
BSH	1660 s	1620 s
BAH	1675 s	1615 s
BPH	1665 s	1625 s
BBH	1670 s	1625 s
BNH	1665 s	1602 s
Ti (BSH) ₂	..	1602 s	1595 s	540 s	460 w	375 m
Ti (BAH) ₂	..	1600 s	1596 m	540 m	458 w	368 m
Ti (BPH) ₂	..	1607 m	1600 m	532 s	461 m	372 m
Ti (BBH) ₂	..	1609 s	1600 s	535 s	460 w	370 w
Ti (BNH) ₂	..	1602 s	1595 s	530 m	460 m	368 m

3250 and 2700–2775 cm⁻¹ supports the involvement of phenolic oxygen in coordination through deprotonation¹¹. From these changes it appears that these ligands are terdentate with coordination taking place through phenolic and enolic oxygen (with deprotonation in both) and azomethine nitrogen. This is further supported by the appearance of a strong band 530–540 and bands around 445–450 and 400–405 cm⁻¹ assignable to ν (Ti–N), ν (Ti–O) (phenolic) and ν (Ti–O) (enolic) vibrations^{6,16}, respectively. It has been observed that titanyl complexes¹⁷ exhibit a strong band ~1090 cm⁻¹ assignable to ν (Ti=O). However, in the present complexes no such band has been observed proving that these complexes do not contain any Ti=O species.

Titanium(IV) is a *d*⁰ system and thus no conclusions regarding its stereochemistry can be drawn from its magnetic and electronic spectral studies. The electronic spectra of all these complexes show a single band in the region 20000–22500 cm⁻¹ which may be due to charge-transfer¹⁸. Magnetic measurements indicate that they are diamagnetic in nature. However, in far infrared region ν (M–N) and

ν (M–X) (X = Cl, Br, etc.), have been of specific use in assigning the stereochemistry of close *d*-shell systems¹⁹. It is known that *cis*-complexes give rise to two metal-ligand (M–N) vibrations while only one such vibration is observed for *trans*-complexes²⁰. In the present case, only one ν (M–N) vibration has been observed in the region (530–540 cm⁻¹) assigned to *trans* six-coordinate octahedral complexes. The metal-oxygen vibrations known to be sensitive to the coordination number and oxidation state²¹ of the central metal ion have consistently been observed around the same frequency (405, 450 cm⁻¹) indicating that these complexes are *trans*-octahedral and the metal atom has the same oxidation state and the same coordination number in these complexes.

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STUDIES ON THE INFLUENCE OF DRAINAGE AS A CULTURAL PRACTICE IN INCREASING RICE YIELDS

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ABSTRACT

Field experiments were conducted to find out the effect of drainage on the growth and yield of rice, grown continuously under a standing water of 5 inches. Plots having drainage provision indicated 28 per cent and 49 per cent increase in rice yield for the varieties CHANDINA and IRATOM-24, respectively, over the rice yield in plots without drainage provision. Analysis of standing water in the field and drain water after an application of 23 kg of nitrogen per hectare on standing water indicated that the applied N is mostly absorbed and retained by soil possibly by diffusion.

INTRODUCTION

IT is well known that highest yields of rice (5–6 tons per hectare) are obtained in Japan and Taiwan and this is usually attributed to the heavy fertilisation and improved cultural practices¹. These practices when applied, however, did not increase the yields significantly in the developing countries, and the highest yield recorded with high yielding varieties was of the order of three tons per hectare. Both Japan and Taiwan have an additional cultural practice, viz., provision of separate drainage channel parallel to irrigation channel in the rice fields^{2,7}. Drainage through the root zone has its own significance in a crop grown with standing water and may contribute significantly to grain yield³⁻⁶.

Experiments both on the field and in the laboratory are, therefore, conducted at the Institute of Nuclear Agriculture with a view to understanding the role of drainage in increasing the rice yield and the effectiveness of broadcasting of fertilizer N on standing water surface in rice fields.

EXPERIMENTAL

A statistically laidout field experiment with and without provision of drainage was initiated on a newly cultivated INA experimental field (Brahmaputra alluvial soils). Treatment A (irrigation with no drainage) and Treatment B (irrigation with drainage) were laid in pair of plots, there being 4 pairs for each treatment. For the purpose of performance study, 2 pairs of each treatment were