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Reactions of Hafnium Tetrachloride with Benzoyl Hydrazones

*V. Verma, S. Kher, and R. N. Kapoor**

Department of Chemistry, University of Delhi, Delhi-110007, India

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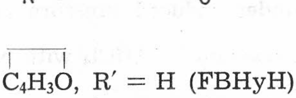
Hafnium tetrachloride reacts with monofunctional bidentate (BHyH) and bifunctional tridentate ($BHy'H_2$) benzoyl hydrazones (derived from the condensation of benzoyl hydrazine with different aldehydes/ketones) in refluxing dichloromethane to form products of the type, $HfCl_3(BHy)$, $HfCl_2(BHy)_2$ and $HfCl_2(BHy')$. These reaction products have been characterized on the basis of elemental analysis, electrical conductance measurements and spectral (infrared and electronic) data.

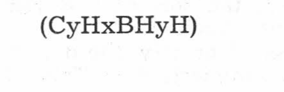
INTRODUCTION

A variety of transition metal complexes of Schiff bases derived from acid hydrazides have been reported[1-7]. Recently, Rao et al.[8] have studied the applications of some of the hydrazone complexes as fungicides. These hydrazones have been of further interest as they are widely used in the treatment of several diseases such as tuberculosis, leprosy and mental disorder[9].

When the terminal NH_2 group of acid hydrazide is condensed with aldehyde/ketone, the proton of the —NH— group becomes more labile and the resulting acid hydrazone can react with metal ions in the keto/enol form[10-13].

In the present work the reactions of mono- and dibasic benzoyl hydrazones (the structures depicted below) with hafnium tetrachloride have been investigated.





(CyHxBHyH)

where R = C_4H_3O, R' = H (FBHyH)
R = C_6H_5, R' = H (BBHyH)
R = p-$(OCH_3)C_6H_4$, R' = H (ABHyH)
R = C_6H_5, R' = CH_3 (AcPhBHyH)
R = C_6H_5, R' = C_6H_5 (BzPhBHyH)

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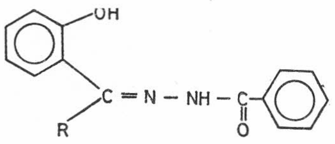
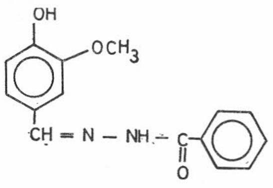
* Author for correspondence





where R = H (SBy'H_2) (VBHy'H_2)
R = CH_3 (AcPh'BHy'H_2)

EXPERIMENTAL

Materials

$HfCl_4$ (Alpha Products) was used without purification. Dichloromethane (BDH) was dried by refluxing it over phosphorous pentoxide and distilled over anhydrous calcium chloride. Hydrazones were synthesised by the condensation of benzoyl hydrazine with aldehydes/ketones in the presence of ethanol[14].

All operations were carried out under anhydrous conditions.

Analytical Methods

Hafnium was estimated gravimetrically as HfO_2 as follows:

The compound was decomposed with conc. HNO_3. The metal was precipitated from this solution by adding ammonium hydroxide. The precipitate was filtered and ignited to HfO_2.

Chlorine was determined as AgCl.

Nitrogen was estimated by Kjeldal's method.

Physical Measurements

The infrared spectra of the complexes were recorded on a Perkin-Elmer 621 spectrophotometer in the 4000—200 cm^{-1} range as KBr pellets. Electrical conductance measurements in DMF were made on an Elico Conductivity Bridge Type CM 82T. Electronic spectra of the complexes were recorded on a Perkin-Elmer 4000A spectrophotometer.

Reaction of Hafnium Tetrachloride with Furfuralbenzoylhydrazone (molar ratio 1 : 1)

To the mixture of hafnium tetrachloride (0.55 g) and furfuralbenzoylhydrazone (0.37 g) was added dichloromethane ($\sim$60 ml). The reaction mixture was refluxed until the evolution of HCl gas ceased. After completion of the reaction the solvent was removed under reduced pressure and an orange brown solid was obtained.

Reaction of Hafnium Tetrachloride with Furfuralbenzoylhydrazone (molar ratio 1 : 2)

The mixture of hafnium tetrachloride (0.54 g) and furfuralbenzoylhydrazone (0.72 g) in dichloromethane (60 ml) was refluxed for about 56 hours. When no more HCl gas evolved, the solvent was removed under reduced pressure and a brown yellow solid was obtained.

For the sake of brevity, the details of the reactions of $HfCl_4$ with other benzoyl hydrazones are summarised in Table I.

RESULTS AND DISCUSSION

The reactions of hafnium tetrachloride with monobasic benzoyl hydrazones such as furfuralbenzoylhydrazone (FBHyH), benzaldehydebenzoylhydrazone (BBHyH), anisaldehydebenzoylhydrazone (ABHyH), cyclohexanonebenzoylhydrazone (CyHxBHyH), acetophenonebenzylhydrazone (AcPhBHyH) and benzophenonebenzoylhydrazone (BzPhBHyH) in 1 : 1 and 1 : 2 molar ratios have

TABLE I

Reactions of Hafnium Tetrachloride with Benzoyl Hydrazones in Dichloromethane

Reactants (Molar ratio)	Refluxing time (hours)	Product and Colour	Analysis % Found (Calcd.)		
			Hf	Cl	N
1	2	3	4	5	6
$HfCl_4$ + FBHyH (1:1)	48	$HfCl_3(FBHy)$ Orange brown	35.00 (35.84)	22.23 (21.36)	5.41 (5.62)
$HfCl_4$ + FBHyH (1:2)	56	$HfCl_2(FBHy)_2$ Brown yellow	27.01 (26.41)	11.10 (10.49)	7.91 (8.29)
$HfCl_4$ + BBHyH (1:1)	46	$HfCl_3(BBHy)$ Cream	34.77 (35.13)	19.98 (20.93)	5.12 (5.51)
$HfCl_4$ + BBHyH (1:2)	65	$HfCl_2(BBHy)_2$ Pale yellow	25.46 (25.65)	10.95 (10.19)	7.85 (8.05)
$HfCl_4$ + ABHyH (1:1)	50	$HfCl_3(ABHy)$ Yellow brown	33.97 (33.17)	19.72 (19.76)	5.03 (5.20)
$HfCl_4$ + ABHyH (1:2)	65	$HfCl_2(ABHy)_2$ Orange brown	24.23 (23.61)	9.23 (9.38)	6.95 (7.41)
$HfCl_4$ + CyHxBHyH (1:1)	55	$HfCl_3(CyHxBHy)$ Cream	35.85 (35.69)	20.48 (21.27)	5.25 (5.60)
$HfCl_4$ + CyHxBHyH (1:2)	65	$HfCl_2(CyHxBHy)_2$ Cream	26.61 (26.25)	9.56 (10.43)	7.92 (8.24)
$HfCl_4$ + AcPhBHyH (1:1)	55	$HfCl_3(AcPhBHy)$ Pale yellow	34.69 (34.18)	19.40 (20.37)	6.04 (5.36)
$HfCl_4$ + AcPhBHyH (1:2)	60	$HfCl_2(AcPhBHy)_2$ Pale yellow	24.58 (24.65)	9.17 (9.79)	7.21 (7.74)
$HfCl_4$ + BzPhBHyH (1:1)	45	$HfCl_3(BzPhBHy)$ Green yellow	29.70 (30.55)	17.50 (18.20)	4.09 (4.79)
$HfCl_4$ + BzPhBHyH (1:2)	70	$HfCl_2(BzPhBHy)_2$ Yellow	21.89 (21.04)	7.60 (8.36)	6.16 (6.61)
$HfCl_4$ + $SBHy'H_2$ (1:1)	50	$HfCl_2(SBHy')$ Yellow	36.21 (36.60)	13.82 (14.54)	5.17 (5.74)
$HfCl_4$ + $VBHy'H_2$ (1:1)	48	$HfCl_2(VBHy')$ Yellow	33.52 (34.48)	12.91 (13.70)	6.32 (5.41)
$HfCl_4$ + $AcPh'BHy'H_2$ (1:1)	55	$HfCl_2(AcPh'BHy')$ Green yellow	36.36 (35.58)	13.43 (14.13)	5.06 (5.58)

been carried out in refluxing dichloromethane. The products of the type, $HfCl_3(BHy)$ and $HfCl_2(BHy)_2$, were obtained according to the following equations:

$$HfCl_4 + BHyH \xrightarrow[\text{reflux}]{CH_2Cl_2} HfCl_3(BHy) + HCl\uparrow$$

$$HfCl_4 + 2BHyH \xrightarrow[\text{reflux}]{CH_2Cl_2} HfCl_2(BHy)_2 + 2HCl\uparrow$$

where $[BHy]^-$ represents the anion of the monobasic benzoyl hydrazone, BHyH.

These complexes are cream to dark brown solids and are insoluble in most of the common organic solvents. Electrical conductance measurements of the few complexes soluble in dimethylformamide show them to be non-electrolytes. All the complexes are hydrolysable in nature.

The reactions of hafnium tetrachloride with salicylaldehydebenzoylhydrazone ($SBHy'H_2$), vanillinbenzoylhydrazone ($VBHy'H_2$) and *O*-hydroxyacetophenonebenzoylhydrazone ($AcPh'BHy'H_2$) in 1 : 1 and 1 : 2 molar ratios in refluxing dichloromethane yielded only products of the type, $HfCl_2(BHy')$:

$$HfCl_4 + BHyH_2 \xrightarrow[\text{reflux}]{CH_2Cl_2} HfCl_2(BHy') + 2HCl\uparrow$$

where $[BHy']^{2-}$ represents the anion of the dibasic benzoyl hydrazone, $BHy'H_2$.

The products are yellow to green yellow solids and are soluble in dimethylformamide. Electrical conductance measurements of these complexes in dimethylformamide show their non-electrolytic nature. The complexes are highly susceptible to hydrolysis.

The elemental analyses and physical data of the reaction products are given in Table I.

Infrared Spectra

Infrared spectra of benzoyl hydrazones (Table II) show a medium to strong band in the region 3260—3150 cm^{-1} assignable to ν(NH) or to ν(NH) combined with hydrogen bonded ν(OH) vibrations as in the case of dibasic hydrazones[3]. The absence of this band in the complexes (Table III) suggests deprotonation of the ligands on complexation with hafnium.

TABLE II

Important Infrared Frequencies of Benzoyl Hydrazones

Benzoyl hydrazone	νNH/ν(NH) + + ν(OH)	Amide-I ν(C=O)	Amide-II ν(CN) + δ(NH)	ν(>C=N—)	ν(C—O) phenolic
Furfuralbenzoylhydrazone (FBHyH)	3260m	1650s	1565m	1625s	—
Benzaldehydebenzoylhydrazone (BBHyH)	3150m	1660s	1570m	1630s	—
Anisaldehydebenzoylhydrazone (ABHyH)	3320m	1645s	1575m	1600s	—
Cyclohexanonebenzoylhydrazone (CyHxBHyH)	3220s	1655s	1535s	1580m	—
Acetophenonebenzoylhydrazone (AcPhBHyH)	3230s	1660s	1555m	1620s	—
Benzophenonebenzoylhydrazone (BzPhBHyH)	3240m	1670s	1510s	1580w	—
Salicylaldehydebenzoylhydrazone ($SBHy'H_2$)	3260s	1665s	1525s	1605s	1250s
Vanillinbenzoylhydrazone ($VBHy'H_2$)	3200s	1645s	1565s	1600s	1265s
2-Hydroxyacetophenonebenzoylhydrazone ($AcPh'BHy'H_2$)	3240s	1645s	1520s	1605s	1280s

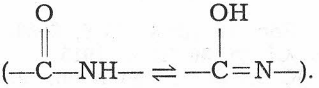
TABLE III

Important Infrared Frequencies of Benzoyl Hydrazone Derivatives of Hafnium Tetrachloride

Compound	ν(>C=N—)[a]	ν(>C=N—)[b]	ν(C—O) phenolic
$HfCl_3(FBHy)$	1590s	1635m	—
$HfCl_2(FBHy)_2$	1590s	1635m	—
$HfCl_3(BBHy)$	1600s	1645m	—
$HfCl_2(BBHy)_2$	1610s	1640m	—
$HfCl_3(ABHy)$	1565m	1630m	—
$HfCl_2(ABHy)_2$	1590m	1630m	—
$HfCl_3(CyHxBHy)$	1545m	1620m	—
$HfCl_2(CyHxBHy)_2$	1545m	1630m	—
$HfCl_3(AcPhBHy)$	1600s	1630m	—
$HfCl_2(AcPhBHy)_2$	1590s	1630m	—
$HfCl_3(BzPhBHy)$	1550m	1600m	—
$HfCl_2(BzPhBHy)_2$	1545s	1590m	—
$HfCl_2(SBHy')$	1595s	1610m	1310m
$HfCl_2(VBHy')$	1590s	1620m	1305s
$HfCl_2(AcPh'BHy')$	1545m	1610m	1320m

[a] coordinated
[b] uncoordinated

The bands observed in the regions 1670—1645, 1575—1510 and 1290—1260 cm^{-1} are assigned to amide-I (ν C=O), amide-II (δ NH + ν CN) and amide-III (δ NH + ν CN) vibrations[15,16], respectively. The appearance of these bands in the ligands indicates that these hydrazones exist in the keto form in the solid state. The bands corresponding to amide vibrations are found to be absent in the infrared spectra of complexes[6] and instead, a new band at 1525—1500 cm^{-1} due to ν (NCO) vibration is observed[4,17]. This shows that the enolized form of the ligands is present in the complexes and that hydrazones are bonded through the deprotonated enolic group.

The medium to strong band observed in the region 1630—1580 cm^{-1} due to ν (C=N) vibration of the azomethine group shows a downward shift of ~35—10 cm^{-1} and is observed in the region 1610—1545 cm^{-1} in the spectra of the complexes. The downward shift of this band is consistent with the coordination of the azomethine nitrogen to the metal atom[2,18-20]. The complexes also show a new band at 1655—1610 cm^{-1} which cannot be assigned to the coordinated carbonyl vibration since this group would disappear on enolization  $(-\overset{\overset{\displaystyle O}{\|}}{C}-NH- \rightleftharpoons -\overset{\overset{\displaystyle OH}{|}}{C}=N-)$. Hence, this band may be attributed to the newly formed uncoordinated azomethine (=C=N—) group[5,21] which seems to have its origin in the conjugate system =C=N—N=C⟨. Such behaviour is diagnostic of the enolisation of the hydrazones.

The spectra of the dibasic hydrazones show a band in the region 1280—1250 cm^{-1} which can be assigned to ν (C—O) (phenolic vibration)[4,19]. This band shows an upward shift and is observed in the region 1320—1305 cm^{-1} in the spectra of complexes, suggesting the bonding of the phenolic oxygen to the metal atom through deprotonation[4,19]. The ν (M—N) and ν (M—O) vibrations, generally absorb in the region 600—400 cm^{-1} [22]. The observed medium to strong intensity bands in the region 555—405 cm^{-1} may be assigned to a mixture of

ν(Hf—N) and ν(Hf—O) vibrations, however, specific assignments are difficult[22,23]. The non-ligand band observed in the region 400—330 cm^{-1} may tentatively be assigned to ν(Hf—Cl) vibration[22-24].

Electronic Spectra

The electronic spectra of a few complexes soluble in dimethylformamide show a single band in the range 27000—26000 cm^{-1} which can be assigned to a charge-transfer transition.

Thus, the complexes obtained from monobasic bidentate ligands may possess five- and six-coordinate stereochemistry whereas for derivatives of dibasic tridentate ligands a five- coordinate structure can be assigned.

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SAŽETAK

Reakcije hafnij(IV)-klorida sa benzoil-hidrazonima

V. Verma, S. Kher i R. N. Kapoor

Hafnij(IV)-klorid reagira s monofunkcionalnim bidentatom (BHyH) i bifunkcionalnim tridentatom ($BHyH_2$) benzoil-hidrazona (izvedenih kondenzacijom benzoil-hidrazina s aldehidima/ketonima) pri refluksiranju diklormetana. Nastali produkti tipa $HfCl_3(BHy)$, $HfCl_2(BHy)_2$ i $HfCl_2(BHy')$ karakterizirani su na temelju elementne analize, mjerenja vodljivosti i spektroskopskih (IC i UV/VID područje) podataka.