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Reactions of Titanium Tetrahalides with Benzoylhydrazine

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As there has been no previous work on the reactions of titanium tetrahalides with hydrazine-derivatives containing carbonyl group such as benzoylhydrazine, it was considered of interest to study the reactions of these Lewis acids with benzoylhydrazine and the results obtained are described in this communication.

Experimental

Titanium tetrahalides and organic solvents used in the present work were purified and made anhydrous employing the standard literature methods. Benzoylhydrazine was prepared from the reaction of ethyl benzoate and hydrazine hydrate and purified by crystallization from benzene, mp 111°C.[1]

Preparation of Complexes. *i) Tetrafluorobis(benzoylhydrazine)titanium(IV).* Solution of benzolyhydrazine (1—5%) in tetrahydrofuran was added gradually with vigorous shaking to the clear solution of titanium tetrafluoride in the same solvent. The homogeneous solution was refluxed for 30 min and the solvent removed till a saturated solution was obtained. Addition of carbon tetrachloride to the above solution yielded a yellow-orange precipitate, which was filtered, washed with a mixture of tetrahydrofuran and carbon tetrachloride and dried under reduced pressure. The complex was recyrstallized from tetrahydrofuran - carbon tetrachloride mixture.

The compound is readily hydrolyzed on exposure

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[1] T. Curtius, *J. Prakt. Chem.*, **50**, (2), 278 (1894).

to atmosphere.

ii) Dichlorobis(benzoylhydrazino)titanium (IV). 40 mmol of titanium tetrachloride, 20 mmol of benzoylhydrazine and 50 m*l* of chloroform were taken in a flask and the suspension refluxed for several hours in an inert atmosphere. The brown solid product formed was filtered, washed with chloroform till free from excess amount of Lewis acid and dried under vacuum. The complex was recrystallized from the tetrahydrofuran-chloroform mixture. The complex is hygroscopic and soluble in tetrahydrofuran.

Dibromobis(benzoylhydrazino)titanium(IV) and diiodobis(benzoylhydrazino)titanium(IV) complexes were prepared in the same way as the chloro complex; iodo complex took a comparatively longer time for drying under reduced pressure. These complexes were also recrystallized form the tetrahydrofuran-chloroform mixture. These complexes are hygroscopic and soluble in tetrahydrofuran too.

The complexes thus prepared were all diamagnetic and the analytical results and general behaviour of the complexes are given in Table 1.

Discussion

An examination of Table 1 shows that titanium tetrafluoride forms adduct of the composition, $TiF_4 \cdot 2BZH$, while other tetrahalides undergo condensation reaction, yielding products of the general formula, $TiX_2(BZ)_2$. When a mixture of benzoylhydrazine and titanium tetrachloride (excess) was kept at 25°C for several days, an unstable 1 : 2 adduct was obtained which lost hydrogen chloride slowly at room temperature but rapidly on heating around 80°C yielding eventually the same condensation product as described above.

The insolubility of titanium tetrahalide complexes of benzoylhydrazine in common organic solvents seriously limits the number of physical measurements that could be carried out for establishing their structures.

The assignment of important absorption bands

TABLE 1. ANALYTICAL DATA AND GENERAL BEHAVIOUR OF THE COMPLEXES

Composition of the solid reaction product	% Found		% Calcd		Colour	Temperature of decomposition (°C)
	Ti	Halogen	Ti	Halogen		
$TiF_4 \cdot 2BZH$	12.84	18.83	12.12	19.19	yellow-orange solid	88—93
$TiCl_2(BZ)_2$	11.88	25.62	11.28	25.00	brown solid	250
$TiBr_2(BZ)_2$	9.74	33.06	10.04	33.44	golden-yellow solid	79—83
$TiI_2(BZ)_2$	8.90	44.75	8.39	44.39	black solid	60—65

TABLE 2. ASSIGNMENT OF IMPORTANT VIBRATIONAL FREQUENCIES OF BENZOYLHYDRAZINE AND ITS COMPLEXES WITH TITANIUM TETRAHALIDES

Compound	Phase	ν(NH) (cm^{-1})	Amide I* (cm^{-1})	Amide II* (cm^{-1})	$\delta(NH_2)$ (cm^{-1})	ν(aromatic C–C) (cm^{-1})	Amide III* (cm^{-1})	ν(N–N) (cm^{-1})
Benzoyl-hydrazine (BZH)	Nujol mull	3285 s 3170 s,b 3130 s	1668 s	1565 s 1518 s	1612 s	1600 s, 1572 s 1492m, 1442 s 1485 s	1345	880m, 915m
	CH_3CN soln.[2]	3350 s	1672 s	—	—	—	1311	—
$TiF_1 \cdot 2BZH$	Nujol mull	3310 w,b 3170 w 3120 w	1658 s 1648 s 1642 s 1630 s 1632 s	1572m 1565m 1552m 1535m	1612m	1596m, 1572m 1495m, 1432 sh 1485m	1360 sh 1338 sh	850m, b 924 w
$TiCl_2(BZ)_2$	Nujol mull	3130m	1632 s 1628 s	1556 s 1542 s	—	1600m, 1586m 1495 w, 1446 s 1488m	1334 w 1338 w	925 w
$TiBr_2(BZ)_2$	Nujol mull	3145 sh	1665 sh 1655 s 1650 s 1620 s	1665 sh 1535 sh 1525 s	—	1595 s , 1575 sh 1650 s , 1435 sh	1320m, b	888 sh 935 sh
$TiI_2(BZ)_2$	Nujol mull	3160 sh	1672 sh 1658 s 1642 s	1590—1535 w,b 1535 w,b	—	1595w, 1465 sh 1445 sh	1346 w	890 w 925 w

* Amide I, carbonyl stretching mode; Amide II, N–H in-plane bending and C–N stretching modes; Amide III, C–N stretching and N–H in-plane bending modes.

TABLE 3. FAR INFRARED SPECTRAL RESULTS OF BENZOYLHYDRAZINE AND THE TITANIUM TETRAHALIDE COMPLEXES

Compound	Tentative assignments			
	ν(Ti–X) (cm^{-1})	ν(Ti–O) (cm^{-1})	ν(Ti–N) (cm^{-1})	Ligand bands (cm^{-1})
Benzoylhydrazine	—	—	—	678 s, 662 s, 605m,b, 345m, 295m, 268 sh, 258m, 247 sh, 240 s
$TiF_4 \cdot 2BZH$	600 s,b, 560 sh, 545 s, 440m, b	510w	—	265w, 255w, 248w, 235w
$TiCl_2(BZ)_2$	395m, b	520w	552 s	680 s, 610 s,b, 345m,b, 268w, 256w, 248w, 235w
$TiBr_2(BZ)_2$	282m	515m	545m	675 s,b, 268w, 258w, 250w, 235w
$TiI_2(BZ)_2$	—	515m	628—535m, b	684m, 346w

in the infrared spectra of benzoylhydrazine and its complexes with titanium tetrahalides has been made on the basis of the reported infrared spectral studies of the titanium tetrahalide complexes of similar bases.

Infrared Spectral Discussion. The spectrum of $TiF_4 \cdot 2BZH$ gives a very broad band in the ν(C=O) region. If 1642 cm^{-1} is taken as the centre of the broad band, a negative shift is obtained in this band indicating coordination through oxygen. A positive shift in one of the N–H stretching bands also supports coordination through oxygen.

A doublet in the spectrum of $TiCl_2(BZ)_2$ with maxima at 1632 and 1629 cm^{-1} and broad bands in the spectra of $TiBr_2(BZ)_2$ and $TiI_2(BZ)_2$ with maxima at 1655, 1650 cm^{-1} and 1658, 1642 cm^{-1} respectively are assigned to amide I. The negative shift in C=O stretching frequency in the complexes indicates coordination through oxygen.

An examination of Table 2 shows that there occurs a decrease in the number of N–H stretching bands in the spectra of above complexes as compared with the parent base. This is probably due to the change of $-NH_2$ group into $>$N–H group as a result of Ti–N bond formation. The appearance of two ν(N–H)[2] bands in acetylbenzoylhydrazine and dibenzoylhydrazine supports the above view point. This is further supported by the disappearance of the $\delta(NH)_2$[2,3] band in the spectra of the complexes.

Since M–O[4,5] and M–N[6] stretching vibrations for a number of transition metal complexes occur in 400—500 cm^{-1} region, it is difficult to assign ν(Ti–N) and ν(Ti–O) unambiguously in the complexes.

Rivest and Jain[7] have assigned ν(Ti–O) mode in the complexes, $TiCl_4 \cdot CH_3CONH_2$ and $TiCl_4 \cdot CH_3CONEt_2$ at 505 and 507 cm^{-1} respectively. The bands occurring in 510—520 cm^{-1} region in the benzoylhydrazine complexes may probably be due to ν(Ti–O) and the bands appearing at 552, 545, and 535—628 cm^{-1} in $TiCl_2(BZ)_2$, $TiBr_2(BZ)_2$ and $TiI_2(BZ)_2$ respectively are tentatively assigned to ν(Ti–N).

The occurrence of ν(Ti–X) in the complexes in the octahedral region[8,9] indicates an octahedral geometry of the complexes.

The infrared spectral studies thus show that BZH acts as a monodentate ligand in $TiF_4 \cdot 2BZH$ coordinating through oxygen and as a bidentate ligand in $TiX_2(BZ)_2$ (X=Cl, Br and I) involving nitrogen, in addition to oxygen, in bond formation with titanium. Two five-membered rings are thus formed around the titanium atom in these complexes.

IR spectral studies also show all the complexes to be octahedral in geometry.

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