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INFRARED AND THERMAL STUDY OF 5,6-BENZOQUINOLINE COMPLEXES OF SOME HIGHER VALENT METAL IONS

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ABSTRACT

The synthesis and physical properties of crystalline ZrO^{2+}, Th^{4+} and UO_2^{2+} complexes of 5,6-benzoquinoline (Benzqn), $ThX_4 \cdot 4Benzqn$ (X = Cl, Br, I, NCS), $Th(NO_3)_4 \cdot 2Benzqn$, $Th(ClO_4)_4 \cdot 6Benzqn$, $ZrOX_2 \cdot 4Benzqn$ (X = Cl, Br, I, NCS), $ZrO(NO_3)_2 \cdot 2Benzqn$, $ZrO(ClO_4)_2 \cdot 6Benzqn$, $UO_2X_2 \cdot 4Benzqn$ (X = Cl, Br, I, NCS), $UO_2(NO_3)_2 \cdot 2Benzqn$ and $UO_2(ClO_4)_2 \cdot 6Benzqn$ are reported, together with their IR spectra, molar conductivity, molecular weights and TGA data. In all the complexes, Benzqn is bonded to metal via nitrogen.

INTRODUCTION

In recent years a number of workers have been interested in complexes with high coordination numbers [1–7]. For a metal ion to achieve a higher coordination number, two conditions are to be satisfied [1–3]; (a) an effective size of the metal ion, and (b) a high positive formal charge of the central metal atom. Zirconium(IV), thorium(IV) and uranium(VI) with atomic radii of 1.45, 1.65 and 1.42 Å, respectively, and a high positive charge fulfil the optimum conditions for high coordination. In view of the variations in stoichiometry from ligand to ligand [4–8] observed for ZrO^{2+}, Th^{4+} and UO_2^{2+} complexes, it was considered worthwhile to study the complexes of these higher valent metal ions with 5,6-benzoquinoline (Benzqn).

EXPERIMENTAL

5,6-Benzoquinoline, purchased from E. Merck, was used without further purification. Lewis acids were obtained or prepared as reported previously [6,7].

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Preparation of complexes

All the complexes were isolated by one of the following methods.

(a) In a typical experiment, an ethanolic solution of lewis acid was mixed with a slight excess of ligand. The reaction mixture was concentrated over a water bath. The concentrated mass was cooled, and an excess amount of diethyl ether was added, to give an oily viscous layer. The viscous layer was separated and washed thoroughly with ether. The viscous mass was dissolved in the minimum amount of absolute ethanol, an excess of diethyl ether was again added, and a precipitate was obtained. The precipitate was filtered, washed with small amounts of ethanol and ether, and dried in vacuo over anhydrous $CaCl_2$.

(b) A solution of lewis acid in ethanol was treated with an excess of lewis base in the same solvent. The mixture was refluxed for ca. 3 h. After cooling the reaction mixture, a solid mass settled. This was filtered, washed with ethanol and ether, and dried as above.

The analyses and physical measurements of the complexes were made as discussed previously [6,7].

RESULTS AND DISCUSSION

The interaction of thorium(IV) salts with Benzqn results in the formation of complexes of the type: $ThX_4 \cdot 4Benzqn$ (X = Cl, Br, I, NCS), $Th(NO_3)_4 \cdot 2Benzqn$ and $Th(ClO_4)_4 \cdot 6Benzqn$. Oxozirconium(IV) salts form the adducts $ZrOX_2 \cdot 4Benzqn$ (X = Cl, Br, I, NCS), $ZrO(NO_3)_2 \cdot 2Benzqn$ and $ZrO(ClO_4)_2 \cdot 6Benzqn$, while the dioxouranium(VI) salts form the adduct with composite on $UO_2X_2 \cdot 4Benzqn$ (X = Cl, Br, I, NCS), $UO_2(NO_3)_2 \cdot 2Benzqn$ and $UO_2(ClO_4)_2 \cdot 6Benzqn$.

The elemental analyses of these complexes are given in Tables 1–3. The complexes are thermally stable and can be stored for a long period at room temperature, except the iodide complexes which decompose to a sticky mass after a few weeks. The complexes are sufficiently soluble in common organic solvents.

The measurement of molar conductance in nitrobenzene (Tables 1–3) reveals that all the halo and nitrato complexes are non-electrolytes. Oxozirconium(IV) and dioxouranium(VI) perchlorato complexes correspond to 1 : 2 electrolytes indicating the presense of both the perchlorate groups outside the coordination sphere. The molar conductance values of $Th(ClO_4)_4 \cdot 6Benzqn$ and $ThI_4 \cdot 4Benzqn$ correspond to 1 : 4 and 1 : 2 electrolytes, respectively.

The molecular weights of the complexes determined by cryoscopic method in nitrobenzene are given in Tables 1–3. The results are in good agreement with the conductance data.

TABLE 1

Analytical data of oxozirconium(IV) complexes of 5,6-benzoquinoline

Complex	Metal (%) found (calc.)	N (%) found (calc.)	C (%) found (calc.)	H (%) found (calc.)	Anion (%) found (calc.)	Λ_m (ohm^{-1} cm^{-2} mol^{-1})	Electrolytic nature	Average molecular weight in $PhNO_2$	Formula weight
$ZrOCl_2 \cdot 4Benzqn$	10.29 (10.17)	6.39 (6.26)	69.98 (69.79)	3.91 (4.02)	8.09 (7.94)	2.79	Non-electrolytic	883	894
$ZrOBr_2 \cdot 4Benzqn$	9.36 (9.25)	5.80 (5.69)	63.62 (63.47)	3.52 (3.66)	16.02 (16.27)	3.16	Non-electrolytic	979	983
$ZrOI_2 \cdot 4Benzqn$	8.58 (8.44)	5.31 (5.19)	58.11 (57.93)	3.22 (3.34)	22.94 (23.58)	4.06	Non-electrolytic	1056	1077
$ZrO(NO_3)_2 \cdot 2Benzqn$	15.56 (15.44)	9.67 (9.50)	53.18 (52.97)	2.86 (3.05)	–	2.16	Non-electrolytic	576	589
$ZrO(NCS)_2 \cdot 4Benzqn$	9.82 (9.63)	9.11 (8.94)	71.65 (71.56)	3.69 (3.83)	11.96 (12.35)	3.79	Non-electrolytic	929	939
$ZrO(ClO_4)_2 \cdot 6Benzqn$	6.79 (6.59)	6.21 (6.08)	67.95 (67.82)	3.79 (3.91)	13.98 (14.42)	54.36	1:2	456	1380

TABLE 2

Analytical data of thorium(IV) complexes of 5,6-benzoquinoline

Complex	Metal (%) found (calc.)	N (%) found (calc.)	C (%) found (calc.)	H (%) found (calc.)	Anion (%) found (calc.)	Λ_m (ohm^{-1} cm^{-2} mol^{-1})	Electrolytic nature	Average molecular weight in $PhNO_2$	Formula weight
$ThCl_4 \cdot 4Benzqn$	21.36 (21.28)	5.06 (5.13)	57.11 (57.24)	3.18 (3.30)	12.82 (13.02)	3.24	Non-electrolytic	1079	1090
$ThBr_4 \cdot 4Benzqn$	18.41 (18.29)	4.30 (4.41)	49.08 (49.21)	2.69 (2.83)	24.86 (25.23)	3.16	Non-electrolytic	1252	1268
$ThI_4 \cdot 4Benzqn$	16.16 (15.93)	3.79 (3.81)	42.69 (42.85)	2.35 (2.47)	34.08 (34.89)	57.92	1:2	480	1456
$Th(NO_3)_4 \cdot 2Benzqn$	27.86 (27.68)	6.59 (6.68)	37.11 (37.23)	2.04 (2.14)	–	2.06	Non-electrolytic	829	838
$Th(NCS)_4 \cdot 4Benzqn$	19.82 (19.66)	9.39 (9.49)	56.72 (56.94)	2.96 (3.05)	19.32 (19.66)	3.96	Non-electrolytic	1162	1180
$Th(ClO_4)_4 \cdot 6Benzqn$	13.78 (13.61)	4.81 (4.92)	54.79 (54.92)	3.04 (3.16)	23.01 (23.35)	99.32	1:4	334	1704

TABLE 3

Analytical data of dioxouranium(VI) complexes of 5,6-benzoquinoline

Complex	Metal (%) found (calc.)	N (%) found (calc.)	C (%) found (calc.)	H (%) found (calc.)	Anion (%) found (calc.)	Λ_m (ohm^{-1} cm^{-2} mol^{-1})	Electrolytic nature	Average molecular weight in $PhNO_2$	Formula weight
$UO_2Cl_2 \cdot 4$Benzqn	24.82 (24.66)	5.96 (5.80)	64.36 (64.66)	3.62 (3.73)	7.12 (7.35)	2.96	Non-electrolytic	949	965
$UO_2Br_2 \cdot 4$Benzqn	22.71 (22.58)	5.52 (5.31)	58.82 (59.20)	3.52 (3.41)	14.81 (15.18)	3.16	Non-electrolytic	1036	1054
$UO_2I_2 \cdot 4$Benzqn	20.91 (20.73)	5.01 (4.87)	54.61 (54.35)	3.21 (3.13)	21.62 (22.12)	4.92	Non-electrolytic	1137	1148
$UO_2(NO_3)_2 \cdot 2$Benzqn	33.90 (33.71)	8.12 (7.93)	44.32 (44.19)	2.65 (2.54)	–	2.03	Non-electrolytic	696	706
$UO_2(NCS)_2 \cdot 4$Benzqn	23.69 (23.56)	8.50 (8.31)	64.32 (64.15)	3.65 (3.56)	11.21 (11.48)	3.98	Non-electrolytic	1003	1010
$UO_2(ClO_4)_2 \cdot 6$Benzqn	15.62 (15.42)	5.56 (5.44)	60.86 (60.66)	3.58 (3.49)	12.36 (12.89)	52.96	1:2	502	1543

Infrared spectra

Detailed IR spectral data of the complexes reported in this paper are available from the authors. The spectra of 5,6-benzoquinoline and its complexes have been studied by various workers [9,10]. Singh [11] has attempted to correlate the vibrational frequencies of quinoline with the equivalent vibrations of pyridine and has used a similar system of numbering the vibrational modes. The assignments to the IR absorption of 5,6-benzoquinoline and its complexes have been made on the basis of the work reported by Singh [11] and others [8,9,12].

Seven bands attributed to C=C and C=N stretchings are ring vibrations occurring in the range 1610–1390 cm^{-1} in the spectra of free 5,6-benzoquinoline. Four absorptions in the same region (8a, 8b, 19a, 19b) have also been identified in the spectrum of the pyridine part. The additional bands in the ligand may thus be associated with the carbocyclic ring, as suggested by Shindo and Tamura [13]. On complexation these frequencies shifted to higher wavenumber, clearly indicating that the ligand is bonded with the metal through the hetero nitrogen atom (not listed).

Other important absorptions, i.e., C–H in-plane deformation, ring breathing and C–H out-of-plane deformations, also show positive shifts on complexation, further confirming the N-bonding. Upon complexation new bands appear in the region 400–350 cm^{-1} which are tentatively assigned to ν(M–N) modes [12,14].

In the perchlorato complexes the very strong ν_3 band and a strong ν_4 band appear in the 1090–1080 and 640–620 cm^{-1} regions, respectively, indicating that tetrahedral symmetry of the perchlorate ion is maintained and it is not bonded to the metal ion [14,15]. In thiocyanate complexes the bands occur at 2080–2050 (νC≡N), 860–830 (νC–S) and 480–460 cm^{-1} (δNCS) which are normally associated with the thermal N-bonded isothiocyanate ion [16,17].

In nitrato complexes the absence of the ν_3 band of ionic nitrate (D_{3h}) around 1360 cm^{-1} and the occurrence of two bands at ca. 1500 (ν_1) and 1300 cm^{-1} (ν_4) clearly suggest the coordination of nitrate ions in these complexes. Further, the bands at ca. 1030 cm^{-1} (ν_2) ca. 820 cm^{-1} (ν_6) and 740 cm^{-1} (ν_3/ν_5) reveal the bidentate nature of nitrate ions in these complexes [14,18–23].

The (M–Cl) stretching vibrations occur in the 290–250 cm^{-1} region [23–25] while the M–Br and M–I stretching vibrations could not be observed in the spectral range studied.

In conclusion, the coordination number (CN) of Zr(IV) is 7, in thorium(IV), the CN varies from 6 to 10 depending upon the nature of anions. The CN of uranium in these complexes is 8.

TABLE 4

Thermal data on oxozirconium(IV) and thorium(IV) complexes of 5,6-benzoquinoline

Complex	Decomposition temp. (°C)		Decomposition product	TG wt. loss (%)		DTG peak (°C)
	Initial	Final		Found	Calc.	
$ZrOCl_2 \cdot 4Benzqn$	170	230	$ZrOCl_2 \cdot 2Benzqn$	41.05	40.04	Endo
	245	280	$ZrOCl_2$	81.32	80.08	
	470	590	ZrO_2	87.92	86.24	Exo
$ZrOBr_2 \cdot 4Benzqn$	165	220	$ZrOBr_2 \cdot 2Benzqn$	38.14	36.41	Endo
	240	280	$ZrOBr_2$	74.14	72.83	
	490	585	ZrO_2	89.31	87.48	Exo
$ZrO(NCS)_2 \cdot 4Benzqn$	175	225	$ZrO(NCS)_2 \cdot 2Benzqn$	39.12	38.12	Endo
	240	280	$ZrO(NCS)_2$	78.52	76.25	
	475	580	ZrO_2	88.09	86.90	Exo
$ZrO(NO_3)_2 \cdot 2Benzqn$	190	305	$ZrO(NO_3)_2$	62.12	60.78	Endo
	470	575	ZrO_2	81.32	79.11	Exo
$ZrO(ClO_4)_2 \cdot 6Benzqn$	170	280	$ZrO(ClO_4)_2 \cdot 4Benzqn$	27.12	25.94	Exo
	475	580	ZrO_2	93.18	91.08	Exo
$ThCl_4 \cdot 4Benzqn$	190	230	$ThCl_4 \cdot 2Benzqn$	33.92	32.84	Endo
	240	390	$ThCl_4$	66.86	65.68	
	420	490	$ThOCl_2$ [a]	64.92	70.73	Exo
$ThBr_4 \cdot 4Benzqn$	180	232	$ThBr_4 \cdot 2Benzqn$	29.32	28.23	Endo
	250	380	$ThBr_4$	57.12	56.46	
	425	500	$ThOBr_2$ [a]	61.91	66.24	Exo
$Th(NCS)_4 \cdot 4Benzqn$	185	235	$Th(NCS)_4 \cdot 2Benzqn$	31.31	30.33	Endo
	280	390	$Th(NCS)_4$	61.76	60.67	
	430	495	$ThO(NCS)_2$ [a]	70.51	69.15	Exo
$Th(NO_3)_4 \cdot 2Benzqn$	210	280	$Th(NO_3)_4$	44.70	42.72	Endo
	425	510	ThO_2	67.19	68.49	Exo
$Th(ClO_4)_4 \cdot 6Benzqn$	190	505	ThO_2	85.51	84.50	Exo

[a] Mixed with ThO_2.

Thermal behaviour

Comparatively less is known about the thermal studies of aromatic amine complexes of metal ions [12,26–29]. In the present studies, TGA of some representative complexes of 5,6-benzoquinoline with oxozirconium(IV) and thorium(IV) have been reported. The thermal results are summarized in Table 4.

Thermogravimetric curves indicate the absence of water of crystallization in the complexes and reveals their non-hygroscopic nature. For other similar amine complexes of the ZrO^{2+} ion, the deligation process of the complexes, $ZrOX_2 \cdot 4Benzqn$ ($X = Cl, Br, NCS$), starts at ca. 165–175°C and is completed at 225 ± 5°C. In this step only two ligand molecules are lost. At 280°C all the ligand molecules have been lost. Finally, at 585 ± 5°C, ZrO_2 is obtained as end product. The TG curve of $ZrO(NO_3)_2 \cdot 2Benzqn$ shows that both the ligand molecules are lost in the 190–305°C temperature range. At 570°C, ZrO_2 is obtained. The TG curve of $ZrO(ClO_4)_2 \cdot 6Benzqn$ indicates that two molecule of ligands are lost at 280°C and a stable intermediate compound, $ZrO(ClO_4)_2 \cdot 4Benzqn$, is obtained. Finally, at 580°C, ZrO_2 is obtained as the end product.

The weight loss values observed in the thermal decomposition of ZrO^{2+} complexes correspond very closely with the general equations.

$$ZrOX_2 \cdot 4Benzqn \rightarrow ZrOX_2 \cdot 2Benzqn \rightarrow ZrOX_2 \rightarrow ZrO_2$$

$(X = Cl, Br, NCS)$

$$ZrO(NO_3)_2 \cdot 2Benzqn \rightarrow ZrO(NO_3)_2 \rightarrow ZrO_2$$

$$ZrO(ClO_4)_2 \cdot 6Benzqn \rightarrow ZrO(ClO_4)_2 \cdot 4Benzqn \rightarrow ZrO_2$$

Similar to ZrO^{2+} complexes the TG curves of $ThX_4 \cdot 4Benzqn$ ($X =$ Cl, Br, NCS) show that the complexes are stable up to 185 ± 5°C, beyond which decomposition starts and continues up to 235°C. Analysis of the thermogram shows that two molecules of ligand are lost at this stage. Further heating to 390°C causes the total loss of ligand molecules. At ca. 500°C, oxohalide species mixed with some ThO_2 are obtained in all cases. Decomposition of $Th(NO_3)_4 \cdot 2Benzqn$ is completed in these steps, while the TG curve of the perchlorato complex shows that the complex starts to decompose at 190°C and continues up to 505°C, after which it corresponds to ThO_2. From the pyrolysis curve it is also found that no stable intermediate perchlorate–Benzqn complexes have been formed.

The thermal stability of Th^{4+} complexes falls in the following order: $NO_3 > Cl > ClO_4 > NCS > Br$.

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