

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: $\text{ThX}_4 \cdot 4\text{Benzqn}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$), $\text{Th}(\text{NO}_3)_4 \cdot 2\text{Benzqn}$ and $\text{Th}(\text{ClO}_4)_4 \cdot 6\text{Benzqn}$. Oxozirconium(IV) salts form the adducts $\text{ZrOX}_2 \cdot 4\text{Benzqn}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$), $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{Benzqn}$ and $\text{ZrO}(\text{ClO}_4)_2 \cdot 6\text{Benzqn}$, while the dioxouranium(VI) salts form the adduct with composite on $\text{UO}_2\text{X}_2 \cdot 4\text{Benzqn}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$), $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{Benzqn}$ and $\text{UO}_2(\text{ClO}_4)_2 \cdot 6\text{Benzqn}$.

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 nitrate 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 $\text{Th}(\text{ClO}_4)_4 \cdot 6\text{Benzqn}$ and $\text{ThI}_4 \cdot 4\text{Benzqn}$ 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 I

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 ·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 ·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 ·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 ·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 ·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 ·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)	Electro- lytic nature	Average molecular weight in PhNO ₂	Formula weight
ThCl ₄ ·4Benzqn	21.36 (21.28)	5.06 (5.13)	57.11 (57.24)	3.18 (3.30)	12.82 (13.02)	3.24	Non- electro- lytic	1079	1090
ThBr ₄ ·4Benzqn	18.41 (18.29)	4.30 (4.41)	49.08 (49.21)	2.69 (2.83)	24.86 (25.23)	3.16	Non- electro- lytic	1252	1268
ThI ₄ ·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 ·2Benzqn	27.86 (27.68)	6.59 (6.68)	37.11 (37.23)	2.04 (2.14)	—	2.06	Non- electro- lytic	829	838
Th(NCS) ₄ ·4Benzqn	19.82 (19.66)	9.39 (9.49)	56.72 (56.94)	2.96 (3.05)	19.32 (19.66)	3.96	Non- electro- lytic	1162	1180
Th(ClO ₄) ₄ ·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})	Electro- lytic nature	Average molecular weight in PhNO_2	Formula weight
$\text{UO}_2\text{Cl}_2 \cdot 4\text{Benzqn}$	24.82 (24.66)	5.96 (5.80)	64.36 (64.66)	3.62 (3.73)	7.12 (7.35)	2.96	Non- electro- lytic	949	965
$\text{UO}_2\text{Br}_2 \cdot 4\text{Benzqn}$	22.71 (22.58)	5.52 (5.31)	58.82 (59.20)	3.52 (3.41)	14.81 (15.18)	3.16	Non- electro- lytic	1036	1054
$\text{UO}_2\text{I}_2 \cdot 4\text{Benzqn}$	20.91 (20.73)	5.01 (4.87)	54.61 (54.35)	3.21 (3.13)	21.62 (22.12)	4.92	Non- electro- lytic	1137	1148
$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{Benzqn}$	33.90 (33.71)	8.12 (7.93)	44.32 (44.19)	2.65 (2.54)	-	2.03	Non- electro- lytic	696	706
$\text{UO}_2(\text{NCS})_2 \cdot 4\text{Benzqn}$	23.69 (23.56)	8.50 (8.31)	64.32 (64.15)	3.65 (3.56)	11.21 (11.48)	3.98	Non- electro- lytic	1003	1010
$\text{UO}_2(\text{ClO}_4)_2 \cdot 6\text{Benzqn}$	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 $\nu(\text{M}-\text{N})$ 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 ($\nu\text{C}\equiv\text{N}$), 860–830 ($\nu\text{C}-\text{S}$) and 480–460 cm^{-1} (δNCS) which are normally associated with the thermal N-bonded isothiocyanate ion [16,17].

In nitrate 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 ·4Benzqn	170	230	ZrOCl ₂ ·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 ·4Benzqn	165	220	ZrOBr ₂ ·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 ·4Benzqn	175	225	ZrO(NCS) ₂ ·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 ·2Benzqn	190	305	ZrO(NO ₃) ₂	62.12	60.78	Endo
	470	575	ZrO ₂	81.32	79.11	Exo
	170	280	ZrO(ClO ₄) ₂ ·4Benzqn	27.12	25.94	Exo
ZrO(ClO ₄) ₂ ·6Benzqn	475	580	ZrO ₂	93.18	91.08	Exo
	190	230	ThCl ₄ ·2Benzqn	33.92	32.84	Endo
	240	390	ThCl ₄	66.86	65.68	
ThBr ₄ ·4Benzqn	420	490	ThOCl ₂ ^a	64.92	70.73	Exo
	180	232	ThBr ₄ ·2Benzqn	29.32	28.23	Endo
	250	380	ThBr ₄	57.12	56.46	
Th(NCS) ₄ ·4Benzqn	425	500	ThOBr ₂ ^a	61.91	66.24	Exo
	185	235	Th(NCS) ₄ ·2Benzqn	31.31	30.33	Endo
	280	390	Th(NCS) ₄	61.76	60.67	
Th(NO ₃) ₄ ·2Benzqn	430	495	ThO(NCS) ₂ ^a	70.51	69.15	Exo
	210	280	Th(NO ₃) ₄	44.70	42.72	Endo
	425	510	ThO ₂	67.19	68.49	Exo
Th(ClO ₄) ₄ ·6Benzqn	190	505	ThO ₂	85.51	84.50	Exo

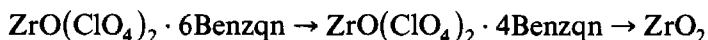
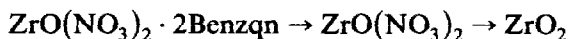
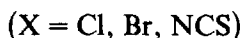
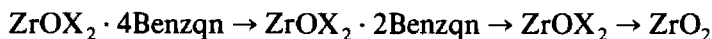
^a Mixed with ThO₂.

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 $225 \pm 5^\circ C$. In this step only two ligand molecules are lost. At 280°C all the ligand molecules have been lost. Finally, at $585 \pm 5^\circ C$, 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.



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 $185 \pm 5^\circ C$, 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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