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Multidentate Azo Dye Complexes of Dioxouranium(VI), Thorium(IV) and Cerium(IV)

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A series of complexes of dioxouranium(VI), thorium(IV) and cerium(IV) has been prepared using neutral 1-(2-pyridyl azo)-2-naphthol (PANH). The neutral ligand and not the anion of the azodye form the complexes. These complexes were characterised by IR, UV, conductivity and elemental analysis. The complexes formed have the composition $[UO_2(HL)_2X_2]$, where $X = NO_3^-$, CH_3COO^-, Cl^-, I^-, SCN^- or 0.5 SO_4^{2-}, $[UO_2L_2]$, $[Th(HL)_2X_4]$ where $X = NO_3^-$, I^- or SCN^- and $[CeL_3(HL)_3]$

INTRODUCTION

Study of azo dye complexes of transition elements have been done in detail, but that of inner transition elements have been rarely studied[1]. In continuation of our earlier work on azodye complexes of some f-block elements[2], here we are reporting the complexes of dioxouranium(VI), thorium(IV) and cerium(IV) with 1-(2-pyridyl azo)2-naphthol (PANH).

EXPERIMENTAL

Preparation of the ligand: The diazonium salt solution obtained from 2-aminopyridine is added to the alkaline solution of β-naphthol solution. The red coloured azo dye obtained was vacuum filtered, washed with water, then with alcohol, finally in ether and dried in vacuum and recrystallized from ethanol (95%).

Preparation of the Complexes:

(i) $UO_2(HL)_2X_2$ ($X = Cl^-, NO_3^-, CH_3COO^-, 0.5\ SO_4^{2-}$) and $Th(HL)_2(NO_3)_4$:

The complexes were prepared by mixing (0.001 M) methanolic solution of $UO_2(NO_3)_2$, UO_2Cl_2, UO_2SO_4, $UO_2(CH_3COO)_2$, $Th(NO_3)_4$ with (0.002 M) warm ligand solution in methanol with constant stirring. Almost immediately a red compound is precipitated out in each case. The resulting mixture was refluxed for 1h., concentrated slowly cooled, filtered, washed with methanol, ether and then dried in vacuum.

(ii) UO_2X_2 and ThX_4 Complexes ($X = SCN^-, I^-$)

Ethanolic solution of $UO_2(SCN)_2$, $Th(SCN)_4$, UO_2I_2, ThI_4 were mixed with 2-mmole ligand solution in ethanol and refluxed for 1h, concentrated slowly, cooled, filtered and dried in vacuum.

(iii) UO_2L_2

The complex was prepared by adding sodium acetate (1g) solution to the ligand solution in ethanol and then to it ethanolic soln of $UO_2(CH_3COO)_2$ was added. Then it was refluxed for some time. A red precipitate was obtained which was filtered washed in ethanol and ether and dried as above.

(iv) $[Ce(HL)_3L_3]$

Ce_2SO_4 (0.005M) was taken in aqueous-ethanolic mixture solution and refluxed for 5 h and on keeping for 2 days it slowly goes into solution. This solution was added to (0.01 M) ligand solution with constant stirring. Almost immediately an orange coloured compound was formed. It was filtered washed in alcohol, ether and dried in vacuum.

RESULTS AND DISCUSSION

The details of the present complexes are given in Table-1. They are stable at high temperature and are insoluble in common organic solvents and sparingly soluble in DMF. The molar conductance values in dilute solution of DMF or CH_3NO_2 in presence of extra amounts of Ph_3PO shows that all the complexes are non-electrolytes.

In the IR spectra of the ligand the bands are usually observed at 3250 cm^{-1} due to ν(OH) vibrations is lowered to 3000 to 3050 cm^{-1} with moderate intensity due to intramolecular O–H – – –N hydrogen bonding[3]. Disappearance of this band in the metal complexes indicates that the neutral phenolic oxygen and not the deprotonated oxygen is bonded to the metal ions. Strong and sharp bands at *ca* 1250 cm^{-1} and 1145 cm^{-1} are the characteristic phenolic ν(C–O) vibrations. Bathochromic shifts of the bands also indicate that the phenolic oxygen is involved in bonding[4]. The bands at 1570 cm^{-1} and 1590 cm^{-1} due to ν(N=N) undergo bathochromic shift to 1550 cm^{-1} in metal complexes indicates that one of the azo nitrogen is bonded to the metal atom[5,6]. The bathochromic shift of ν(C–N) at 1200 cm^{-1} in ligand to 1185 cm^{-1} also indicates co-ordination through the azo nitrogen atom. The pyridyl nitrogen atom is not involved in bonding due to unstability of a 4-membered ring formed with the metal atom[7].

The IR bands due to the UO_2^{2+} group are observed at around 910 and 815 cm^{-1} as sharp bands corresponding to the asymmetric streching frequency, ν_{as}(U–O) and the symmetric streching frequency ν_s(U–O) respectively. These observation indicate that the UO_2 moiety in all cases is virtually linear[8].

The IR spectra of uranyl nitrate complex shows no absorption bands near 1380 cm^{-1}, where the free nitrate ion is known to absorb. Other bands at 1480, 1290, 1030 and 740 cm^{-1} corresponding to the ν_1, ν_4, ν_2 and ν_3 vibrations respectively of unidentate nitrate group[9]. Thus the uranium have a co-ordination number of 8 and six atoms around the axial position of the linear UO_2 group. Thorium nitrato complex shows bands at 1520, 1440, 1275, 1205, 905 and 805 cm^{-1} agree with the frequencies reported for bidentate nitrate group. The absence of a band at 1380 cm^{-1} indicates that no ionic nitrate groups are present.

TABLE 1
ANALYTICAL DATA AND KEY IR FREQUENCIES (cm^{-1}) OF THE COMPLEXES

Compound/ Colour.	M. pt. (°C)	Found (Calc.)%				ν(O–H)	ν(C–N)	ν(C–O)	ν(–N=N–)	Polyatomic anion modes (cm^{-1})
		N	C	H	M					
Ligand PANH(HL), Red	111	16.88 (16.88)	72.24 (72.28)	4.19 (4.41)	—	3030br	1200s	1250s 1145s	1570s 1590s	—
$[UO_2(HL)_2(NO_3)_2]$ Maroon.	>250	12.80 (12.55)	40.50 (40.35)	2.10 (2.46)	26.80 (26.68)	3050m	1187s	1245s 1135s	1550s 1590s	1482s, 1480s, 1292s, 1290s, 1030s, 740s.
$[UO_2(HL)_2(CH_3COO)_2]$ Maroon.	>250	9.10 (9.48)	46.40 (46.04)	2.30 (2.53)	26.50 (26.86)	3060s	1187s	1245s 1135s	1550s 1590s	1615s, 1380s, 1030s, 740s.
$[UO_2L_2]$ Maroon.	>250	10.60 (10.96)	46.70 (46.99)	2.20 (2.61)	30.70 (31.07)	3055s	1185s	1245s 1135s	1550s 1590s	—
$[UO_2(HL)_2SO_4]$ Maroon.	>250	9.50 (9.72)	41.40 (41.66)	2.40 (2.54)	28.06 (27.54)	3060s	1185s	1240s 1130s	1550s 1590s	1150s, 1120s, 1100s, 1090s, 1035s, 635s.
$[UO_2(HL)_2Cl_2]$ Maroon.	>250	9.80 (10.01)	42.50 (42.90)	2.40 (2.62)	28.82 (28.36)	3050s	1185s	1245s 1135s	1550s 1590s	—
$[UO_2(HL)_2(SCN)_2]$ Maroon.	>250	12.30 (12.66)	43.10 (43.43)	2.20 (2.48)	26.80 (26.92)	3045s	1185s	1240s 1130s	1565s 1590s	2040s, 820s.
$[UO_2(HL)_2I_2]$ Maroon.	>250	8.40 (8.21)	35.10 (35.22)	1.80 (2.15)	23.10 (23.28)	3055s	1185s	1245s 1135s	1560s 1590s	—

Compound/ Colour.	M. pt. (°C)	Found (Calc.)%				ν(O–H)	ν(C–N)	ν(C–O)	ν(–N=N–)	Polyatomic anion modes (cm^{-1})
		N	C	H	M					
$[Th(HL)_2(NO_3)_4]$ Red.	>250	13.90 (14.31)	37.03 (36.80)	1.90 (2.24)	23.60 (23.72)	3100s	1190s	1210s 1135s	1560s 1590s	1520s, 1440s, 1275s, 1205s, 905s, 805.
$[Th(HL)_2(SCN)_4]$ Red.	>250	14.16 (14.55)	42.10 (42.41)	2.00 (2.28)	24.26 (24.11)	3040s	1190s	1245s 1130s	1560s 1590s	2040s, 830s.
$[Th(HL)_2I_4]$ Red.	>250	6.4 (6.78)	29.40 (29.07)	1.00 (1.77)	18.60 (18.73)	3040s	1190s	1245s 1130s	1550s 1590s	—
$[CeL_3(HL)_3]$ Orange.	>250	15.78 (15.45)	66.40 (66.21)	4.20 (3.86)	8.30 (8.58)	3050s	1190s	1245s 1135s	1560s 1590s	—

Thus all the four nitrate groups are bonded in a bidentate manner.[10,11] In both of $[UO_2(HL_2)(SCN)_2]$ and $[Th(HL)_2(SCN)_4]$ these thiocyanato complexes exhibits sharp bands at 2040 cm^{-1} and a sharp band at 820 cm^{-1} (830 cm^{-1} for Th complex) corresponding to $\nu(C\equiv N)$ and $\nu(C-S)$ respectively. This suggests that the thiocyanate is co-ordinated through nitrogen atom.[12] The bands at 1150, 1120, 1100, 1090, 1035 and 635 cm^{-1} confirm that the sulphato group is bonded in bidentate manner.[13]

It is interesting to note that one of the phenolic hydrogen is lost when uranyl acetate reacts with the ligand (1:1) in presence of sodium acetate where as the ligand did not loose the phenolic hydrogen and forms an acetate complex in absence of sodium acetate. This fact is supported by conductance measurement and IR data. The observed bands at 1615, 1380, 1030 and 740 cm^{-1} corresponding to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ respectively,[14,15] where as in the neutral complex many of these bands are absent.

The conductivity of the halo complexes in various organic solvents shows a stable M-X bond. In all cases conductivities were measured after adding extra triphenyl phosphine oxide ligand and observed that the results are not effected. This clearly indicates that all the halogens are involved in covalent bonding.[16] However the thorium iodide complex undergoes decomposition when it comes in contact with air.

It is interesting to note that cerium forms a neutral complex with three deprotonated ligands and three protonated ligands. The stoichiometry of the complex was confirmed from analytical data. Thus cerium forms a compound having an unusual coordination number of 12.

The electronic spectra of the ligand and the complexes shows that the uranyl complexes invariably exhibit band at 340 to 500 nm due to vibronic structure and the equatorial ligand has minor influence on the spectrum.[17,18] In all the complexes bands in the region 290, 370 and 460 nm were observed. However the typical band of the UO_2^{2+} group which is expected around 390–450 nm seems to be overlapped by the fairly strong ligand to neutral charge transfer bands.[19,20]

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