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Synthesis and Characterization of Thorium(IV) Complexes of 2,3-dimethyl-1-phenyl-4-(2-hydroxy-5-methyl phenyl azo)-pyrazol-5-one

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Five new Th(IV) complexes of an azo dye, 2,3-dimethyl-1-phenyl-4-(2-hydroxy-5-methyl-phenylazo)-pyrazol-5-one (cresol azo antipyrine, CAAPH) have been prepared and characterized by elemental analysis, magnetic moment and conductance measurements, IR and NMR spectral studies. The thermal behaviour of one of the complexes has also been examined. On the basis of the above studies, the complexes confirm the composition [$Th(CAAPH)_2X_4$], where X = NO_3^-, NCS^-, Cl^-, I^- or ClO_4^-. The X-ray powder diffraction patterns of the complex [$Th(CAAPH)_2Cl_4$] has been examined and found to be orthorhombic with the unit cell dimensions a = 15.4185 Å, b = 9.7577 Å and c = 7.2784 Å.

Key Words: **Synthesis, Characterisation, Thorium(IV), Complexes, 2,3-Dimethyl-1-phenyl-4-(2-hydroxy-5-methyl-phenyl-azo)-pyrazol-5-one.**

INTRODUCTION

The coordination chemistry of Th(IV) is very interesting. The high charge on Th(IV) ion along with its effective ionic size (99 ppm) enables it to form complexes with high coordination numbers[1, 2].

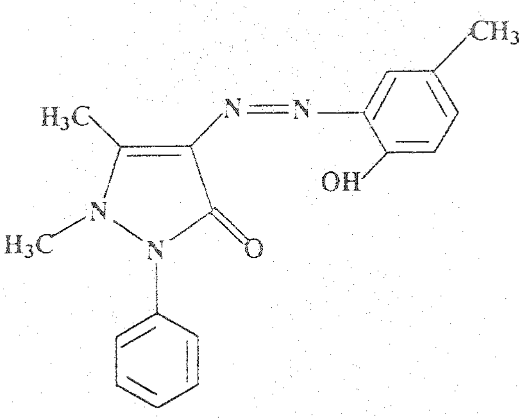
A number of complexes ofazodyes derived from 4-amino antipyrine with some *d*-block and *f*-block metal ions have been reported[3–8]. We have synthesised and characterized five new Th(IV) complexes of the potential tridentate ligand 2,3-dimethyl;-1-phenyl-4-(2-hydroxy-5-methyl phenyl azo)-pyrazol-5-one(cresol azo antipyrine CAAPH), derived from biologically active molecule, 4-amino-antipyrine[4, 9, 10, 11]. CAAPH is a potentially tridentate monobasic ligand (Fig. 1).

EXPERIMENTAL

4-Amino antipyrine (Fluka, Switzerland), *p*-cresol (Loba-Chemie, Mumbai), $Th(NO_3)_4 \cdot 5H_2O$ (LobaChemie) were used as supplied. All other chemicals used were of BDH AR grade.

Preparation of the Ligand: The ligand was prepared from 4-amino antipyrine and *p*-cresol by diazotization and coupling as described in literature[12].

Preparation of the Complexes: Methanolic solutions of the metal salt



CAAPH

Fig. 1. Structure of 2,3-dimethyl-1-phenyl-4-(2-hydroxy-5-methyl phenyl azo)-pyrazol-5-one (CAAPH)

(1 mmol) were added to hot solutions of the ligand (2 mmol) and refluxed for *ca.* 4 h. On cooling, the precipitated complexes were filtered off, washed with benzene followed by ether and dried *in vacuo* over P_4O_{10}.

For the preparation of the thiocyanato and perchlorato complexes, a methanolic solution of thorium nitrate (1 mmol) containing *ca.* 0.3 g NH_4CNS/2–3 drops of $HClO_4$, as the case may be, was mixed with hot methanolic solution of the ligand (2 mmol) and refluxed for *ca.* 4 h. The solid separated was filtered, washed with benzene followed by ether and dried *in vacuo*.

The metal salt solution for preparing the iodo complex was obtained by mixing methanolic solutions of thorium nitrate (1 mmol) and potassium iodide (0.4 g) and filtering off the KNO_3. The resulting solution was concentrated and added in drops to the hot methanolic solution of the ligand (2 mmol) and refluxed for *ca.* 4 h. The complex formed was filtered, washed with benzene, followed by ether and dried *in vacuo*.

For the preparation of thorium tetrachloride, an aqueous solution of thorium nitrate was treated with aqueous ammonia. The thorium hydroxide formed was filtered, washed with ether and dried. The $Th(OH)_4$ so obtained was dissolved in 1 : 1 HCl and evaporated to dryness. A methanolic solution (1 mmol) of the metal chloride was added to a hot methanolic solution of the ligand and refluxed for *ca.* 4 h. The complex formed was filtered, washed with benzene, followed by ether and dried *in vacuo*.

The metal, halogen, sulphur and perchlorate in the complexes were estimated by standard methods[12, 13]. Elemental analysis (C, H, N) was carried out at RSIC, CDRI, Lucknow. The molar conductances of the complexes in $C_6H_5NO_2$, CH_3CN and CH_3OH (*ca.* 10^{-3} M) were measured at 300 ± 1 K using an Elico conductivity bridge type CM82T with a dip type cell (ec 0.03) fitted with platinum electrodes (cell constant 0.995 cm^{-1}). The IR spectra of the ligand and the complexes were recorded in the region 4000–400 cm^{-1} on a Jasco FTIR 430 spectrophotometer using KBr pellets. X-ray powder diffraction patterns of one of the complexes were recorded using Philips X-ray PW 1710 diffractometer.

The magnetic susceptibilities at room temperature (300 ± 2 K) were measured on a Gouy balance using $[HgCo(NCS)_4]$ as the calibrant[14]. Diamagnetic corrections for various atoms and structural units were computed using Pascal's constants[15].

RESULTS AND DISCUSSION

All the complexes are dark brown in colour and non-hygroscopic. The complexes are moderately soluble in methanol, ethanol and insoluble in benzene and ether.

The analytical data of the complexes (Table-1) correspond with the composition $[Th(CAAPH)_2X_4]$ where CAAPH is a bidentate ligand and $X = NO_3^-$, NCS^-, Cl^-, I^- or ClO_4^-. In some complexes, mixed anions are present. The molar conductances show that all the complexes are nonelectrolytes[16–18].

All the Th(IV) complexes are found to be diamagnetic as expected.

The IR spectra of the ligand show a broad band of medium intensity *ca.* 2930 cm^{-1}, assigned to hydrogen bonded OH group[19]. This band disappears in the spectra of all the complexes. Instead, a broad band of medium intensity is observed at *ca.* 3400 cm^{-1}, indicating the presence of free OH group and its non-involvement in coordination to the metal ion. The $\nu(C{=}O)$ found at 1665 cm^{-1} in the spectrum of the ligand shows a downward shift by 60 cm^{-1} in the spectra of all the complexes confirming the involvement of (C═O) group in complexation[20]. The vibrational band observed at 1450 cm^{-1} assigned to $\nu(N{=}N)$ of the ligand is shifted by 20 cm^{-1} in the spectra of all the complexes suggesting the participation of the azo group in coordination with the metal ion[21, 22]. Thus the ligand is coordinated to the metal ion through the carbonyl oxygen and one of the azo group nitrogens only, showing a neutral bidentate behaviour during complexation.

The IR spectra of the nitrate complexes are suggestive[23] of monodentately coordinated nitrate group (ν_4 *ca.* 1490, ν_1 *ca.* 1385 and ν_2 *ca.* 1025 cm^{-1}). The N-coordinated nature[24] of the thiocyanate group is indicated by the $\nu(C{-}N)$ (2050 cm^{-1}), $\nu(C{-}S)$ (754 cm^{-1}) and $\delta(NCS)$ (470 cm^{-1}). For the perchlorato complex the three bands at 1120, 1077 and 630 cm^{-1} may be assigned to ν_4, ν_1 and ν_3 modes of unidentately coordinated ClO_4^- ion[25] (Table-2).

In the ^1H NMR spectrum of the ligand, CAAPH, the signal due to $C{-}CH_3$ group appears as a sharp singlet (3H) at δ 2.30 ppm. The $N{-}CH_3$ signal is observed as another singlet at δ 3.10 ppm. Another singlet at δ 3.4 ppm is assigned to $C{-}CH_3$ group in the phenyl ring. The signal due to the aromatic protons appears as a multiplet between δ 7.04 ppm and δ 7.59 ppm. A singlet at δ 8.1 ppm is assigned to hydrogen bonded phenolic proton.

All the signals observed in the ^1H NMR spectrum of CAAPH are retained in the spectrum of the complex $[Th(CAAPH)_2(NO_3)_4]$. The presence of a signal at δ 8.15 ppm in the complex is due to the phenolic proton. This indicates the nonparticipation of the OH group during coordination supporting the IR spectral evidence.

Thermal analysis ofthe complex $[Th(CAAPH)_2(NO_3)_2(NCS)_2]$ was carried out

TABLE-1

ANALYTICAL AND CONDUCTIVITY DATA OF COMPLEXES

Complex	Analysis %: Found (Calcd.)							Molar conductance (Ω^{-1} cm^2 mol^{-1})					
	Th	C	H	N	Cl/I	ClO_4	S	$C_6H_5NO_2$		CH_3CN		CH_3OH	
								Conc.×10^{-3} M	Cond.	Conc.×10^{-3} M	Cond.	Conc.×10^{-3} M	Cond.
$[Th(CAAPH)_2(NO_3)_4]$	20.45 (20.63)	38.23 (38.41)	3.15 (3.20)	4.82 (4.98)	–	–	–	0.987	5.8	0.899	38.2	0.981	53.8
$[Th(CAAPH)_2(NO_3)_3I]$	19.15 (19.50)	36.11 (36.31)	3.00 (3.05)	3.41 (3.53)	10.11 (10.67)		–	0.991	5.2	0.990	39.3	0.896	48.2
$[Th(CAAPH)_2(NO_3)_2(NCS)_2]$	20.57 (20.77)	40.68 (40.84)	3.18 (3.22)	4.95 (5.01)	–	–	5.61 (5.73)	0.980	4.4	0.981	28.1	0.991	38.3
$[Th(CAAPH)_2(NO_3)_2(ClO_4)_2]$	19.23 (19.34)	35.88 (36.01)	2.98 (3.00)	2.26 (2.33)	–	16.41 (16.58)	–	0.985	8.1	0.991	47.1	0.989	57.3
$[Th(CAAPH)_2Cl_4]$	22.58 (22.78)	42.19 (42.42)	3.41 (3.53)	–	13.72 (13.92)	–	–	0.979	5.1	0.968	29.2	0.995	30.1

by TG and DTG techniques in static air at a heating rate of 10°C per min. The TG plateau up to 170°C shows its stability and the complex starts decomposition after this temperature. There are three stages of decomposition as shown by the DTG peaks at 189°, 442° and 566°C. The TG curve shows a second plateau after 580°C. This indicates the completion of the decomposition. The decomposition at 189°C is due to the dissociation of the two thiocyanate moiety, making a mass loss of 10%. The decomposition continues with a gradual decrease in weight and at 442°C decomposition of the organic moiety takes place, making a mass loss of 68%. The third stage of decomposition takes place at 566°C with mass loss of 76%. The residual mass is about 23.6% (theoretical 23.29%) which has been ascribed to the oxidative decomposition to give ThO_2 as the ultimate residue.

TABLE-2
KEY IR SPECTRAL BANDS (cm^{-1}) OF CAAPH AND ITS Th(IV) COMPLEXES

CAAPH	$[Th(CAAPH)_2(NO_3)_4]$	$[Th(CAAPH)_2(NO_3)_3I]$	$[Th(CAAPH)_2(NO_3)_2(NCS)_2]$	$[Th CAAPH)_2(NO_3)_2(ClO_4)_2$	$Th(CAAPH)_2Cl_4]$	Assignments
	3410 bm	3410 bm	3400 bm	3440 bm	3410bm	ν(O—H) free
2930 bm	–	–	–	–	–	ν(O—H) hydrogen bonding
			2045 s	–	–	ν(C—N) of NCS^-
1665 vs	1605 vs	1620 s	1595 s	1603 s	1603 s	ν(C=O) pyrazolone
	1490 s	1490 s	1494 s	1493 s		$\nu_4(NO_3^-)$
1450 s	1430 s	1385 s	1430 s	1428 s	1425 s	ν(N=N)
	1384 s	1430 s	1385 s	1384 s		$\nu_1(NO_3^-)$
		1385 s		1120 s		$\nu_4(ClO_4^-)$
				1077 s		$\nu_1 ClO_4^-$
	1025 m	1025 m	1028 m	1025 m		$\nu_2(NO_3^-)$
			754 m			ν(C—S) of N bonded NCS
				631 m		$\nu_3(ClO_4^-)$
			472 m			δ(NCS)

X-ray diffraction study of the complex $[Th(CAAPH)_2Cl_4]$ has been carried out and was indexed using Hesse and Lipson's procedure[26, 27]. The results show that the complex belongs to the orthorhombic crystal system, having unit cell dimensions a = 15.4185 Å, b = 9.7577 Å and c = 7.2784 Å.

On the basis of the above evidences the complexes confirm the structure as $[Th(CAAPH)_2X_4]$ where X = NO_3^-, NCS^-, Cl^-, I^- or ClO_4^- with coordination number 8 shown by Th(IV) in these complexes (Fig. 2).

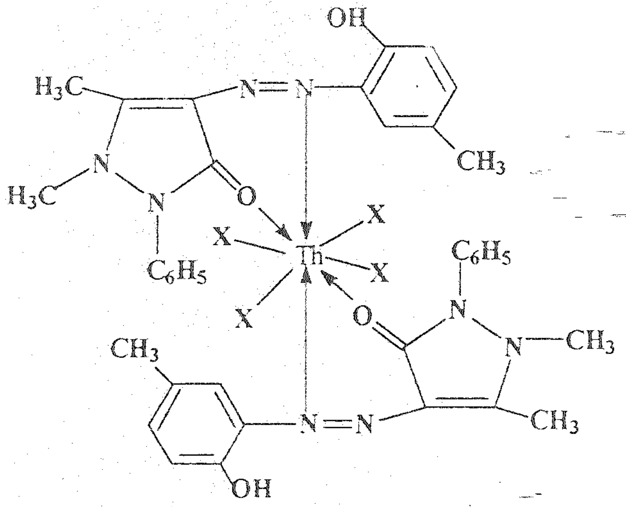


Fig. 2. [Th(CAAPH)$_2$X$_4$]

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