Thorium(IV) complexes with some *ortho*-substituted Schiff base ligands

Wissam I. Azeez
Chemistry Department, Mosul University, Mosul (Iraq)

(Received January 31, 1990; revised May 29, 1990)

Abstract

Thorium(IV) thiocyanate, chloride and nitrate complexes with Schiff bases L (*ortho*-$XC_6H_4CH=NC_6H_4COOH$) derived from *o*-XC_6H_4CHO and 2-carboxyaniline have been prepared. The ligands acted as deprotonated uninegative tridentate molecules when X = OH or deprotonated uninegative bidentate ones when X = Cl, OCH_3 or NO_2. The resulting thorium(IV) centres in the complexes are therefore eight- or six-coordinated, respectively.

Introduction

Several Schiff base complexes of thorium(IV) and dioxouranium(VI) have been reported in recent years [1–9]. It seems from the literature that thorium(IV) complexes with Schiff bases derived from *ortho*-carboxyaniline-*N*-X-benzalidine have not been prepared so far. In this paper the synthesis and characterization of Th(IV) thiocyanate, chloride and nitrate complexes with *ortho*-X-C_6H_4CHO and 2-carboxyaniline where X = Cl, OCH_3 and NO_2 are reported.

Experimental

Materials and measurements

Hydrated thorium(IV) chloride and nitrate were B.D.H. reagent grade. Thorium thiocyanate solutions were prepared as described previously [10]. *ortho*-Carboxyaniline-*N*-salicylidene and *ortho*-carboxyaniline-*N*-X-benzylidene (X = OCl, OCH_3 and NO_2) ligands were synthesized by established procedures [11, 12]. The complexes were prepared by mixing a warm ethanolic solution of the appropriate thorium salt with the ligand in ethanol medium (1:2.5 ratio) under a dry nitrogen atmosphere using a glove box. In most cases the complexes appeared almost immediately on stirring but in some cases refluxing for *c.* 30 min was necessary. The solution was filtered, washed with ethanol then diethyl ether and finally dried *in vacuo* for *c.* 6 h at 120 °C.

C, H and N microanalyses were carried out using a CHN analyser type 1106 (Carlo Erba). Thorium was determined by the gravimetric method [13]. Analytical results are summarised in Table 1.

Conductance measurements were made at *c.* 300 K in $PhNO_2$ solution and $MeNO_2$ (*c.* 10^{-3} M) with a conductivity bridge type MCl.

IR spectra (Nujol mulls) in the 400–4000 cm^{-1} region were recorded using a Pye UNICAM S.P.3 2000 spectrometer.

UV–vis spectra were recorded using a Pye UNICAM S.P.800 spectrophotometer.

Raman spectra were recorded in solution and were carried out by the Chemistry Department of Manchester University, U.K.

Results and discussion

The complexes isolated are listed in Tables 1 and 2 together with their characterization data. The compounds have an intense orange–yellow colour, high melting points (>240 °C) and the electrical conductance values in $PhNO_2$ and $MeNO_2$ solutions confirmed the non-electrolyte nature of the complexes [14].

The electronic spectra in methanol are similar to each other with regard to band frequencies, shape and relative intensities. All these compounds in solution could, therefore, have similar structures.

The IR spectra of the ligands and the complexes were also investigated. The ligands show two bands in the regions 1592–1620 and 1372–1390 cm^{-1} which may be assigned to $\nu_{as}(COO^-)$ and $\nu_{sym}(COO^-)$, respectively. On complexation these occur at 1568–1590 and 1383–1395 cm^{-1}, respectively; the

0020-1693/90/$3.50

TABLE 1. Analytical results, yields, melting points (m.p.) and molar conductance data

ortho X in Th complex	Found (calc.) (%)				Ω_m (Ω^{-1} cm^2 mol^{-1})		m.p. (°C)	Yield (%)
	C	H	N	Th	$PhNO_2$	$MeNO_2$		
$Th(NCS)_2L_2$								
OH	43.7	2.5	6.7	27.9	2.3	40	248	60
	(43.5)	(2.4)	(6.8)	(28.0)				
Cl	41.7	2.0	6.7	27.0	2.1	34	250–254^a	62
	(41.6)	(2.1)	(6.5)	(26.8)				
OCH_3	45.0	2.9	7.4	27.0	3.3	45	242–245^a	70
	(44.9)	(2.8)	(7.5)	(27.1)				
NO_2	41.0	1.9	9.3	26.5	5.6	42	245	65
	(40.8)	(2.0)	(9.0)	(26.3)				
$ThCl_2L_2$								
OH	43.1	2.5	3.5	29.4	3.1	12	260–264	82
	(42.9)	(2.6)	(3.6)	(29.6)				
Cl	40.8	2.1	3.5	28.5	1.0	10	255	75
	(41.0)	(2.2)	(3.4)	(28.3)				
OCH_3	44.1	3.9	3.2	28.7	3.5	11	248	78
	(44.4)	(3.0)	(3.5)	(28.6)				
NO_2	39.9	2.0	6.6	27.5	6.2	9	260^a	80
	(40.0)	(2.1)	(6.7)	(27.6)				
$Th(NO_3)_2L_2$								
OH	40.9	2.5	6.8	28.0	2.6	25	248^a	73
	(40.2)	(2.4)	(6.7)	(27.8)				
Cl	38.8	2.3	6.7	26.4	1.2	22	252	78
	(38.5)	(2.1)	(6.4)	(26.6)				
OCH_3	41.9	2.6	6.4	27.0	4.0	18	250–255	78
	(41.7)	(2.8)	(6.5)	(26.9)				
NO_2	37.7	1.9	9.2	27.0	4.2	20	245	68
	(37.6)	(2.0)	(9.4)	(26.9)				

^{a}Decomposed.

shift of $\nu(COO^-)$ of 185–195 cm^{-1} indicates that the carboxylate group present is acting as a monodentate group [15]. A strong band in the region 1620–1670 cm^{-1} for the uncomplexed ligand is characteristic of the azomethine group, C=N. On complexation this band splits into two, indicating nitrogen–metal bonding [16, 17]. The frequency shift ν(C=N) to higher wave number (5–20 cm^{-1}) which occurs upon complexation may arise from coordination effects and not from the nature of the substituent group of the Schiff base. The more powerful electron withdrawing X in such Schiff base ligands would tend to lower the ν(C=N) frequency in the CH=N moiety due to the relative decrease in the bond order of the C–N link. The two absorption bands at 1195 and 1320 cm^{-1}, due to the phenolic CO stretching and OH bending vibrations, respectively, are shifted to lower frequency indicating coordination via the phenolic CO group. Hence the tridentate nature of this ligand has been achieved through the hydroxy, carboxyl and imine nitrogen groups of the Schiff base ligand when X = OH, which acts as a deprotonated uninegative tridentate ligand with the thorium atom. The other ligands in which X = Cl, OCH_3 and NO_2 are, however, coordinated as deprotonated uninegative bidentate molecules. The nitrato complexes exhibit features at 1460, 1280, 1045, 820 and 730 cm^{-1} which indicate unidentate coordination (C_{3v}) of the nitrato group [18]. The thiocyanate complexes exhibit bands at 2040 (vs) and 840 cm^{-1}, corresponding to ν(C=N) and ν(C–S) of N-coordinated terminally bonded isothiocyanate. The symmetry may be deduced from the activity of ν(C–N) in the IR and Raman spectra. The symmetry likely from these complexes is either C_{2h} or C_{2v} (see Table 3).

The results in Table 2 indicate that the thiocyanate complexes seem to have one IR active and one

TABLE 2. Vibrational frequencies (cm^{-1}) of the ligands and their complexes[a]

L(complex)	Phenolic		ν_{as}(COO$^-$)	ν_{sym}(COO$^-$)	ΔCOO	ν(C=N)	ν(SCN) Raman line
	δ(OH)	ν(CO)					
$Th(NCS)_2L_2$							
OH	1320w	1195m	1600s	1390m		1620s	2060vs, 2025s pol
	1305w	1185w	1568w	1385m	183	1620s, 1640m	
Cl			1620m	1385s		1670s	2050vs, 2020s pol
			1570m	1380m	190	1605s, 1640m	
OCH_3			1595s	1378m		1625s	2060vs, 2020s pol
			1580w	1385s	195	1615s, 1630m	
NO_2			1592s	1372m		1640s	2050vs, 2025s pol
			1575m	1390m	185	1625s, 1635m	
$ThCl_2L_2$							
OH	1310mbr	1190w	1588m	1390br		1625s, 1635	
Cl			1590m	1395s	195	1625s, 1620m	
OCH_3			1590w	1383m	197	1620m	
NO_2			1590m	1390–1420br		1625s, 1635sh	
$Th(NO_3)_2L_2$							
OH	1300mbr	1178w	1590m	1390–1420br		1610s, 1640m	
Cl			1578s	1390–1420br		1620m, 1650m	
OCH_3			1588m	1390–1410mbr		1625m–1635m	
NO_2			1590m	1385m	185	1625s	

[a]s = strong; vs = very strong; m = medium; mbr = medium broad; br = broad; pol = polarized.

TABLE 3. Calculated C—N stretching modes of (a) C_{2h} and (b) C_{2v} symmetries[a]

(a) Mode C_{2h} activity

Ag	B_4	*N*	*R*	*P*	*IR*	*C*
R(P)	IR	2	1	1	1	0

(b) Mode C_{2v} activity

A_1	B_1	*N*	*R*	*P*	*IR*	*C*
R(P), IR	R, IR	2	2	1	2	0

[a]*N* = number of normal modes, *R* = number of Raman active modes, *P* = polarized Raman active modes, *IR* = number of infrared active modes, *C* = number of coincidences.

Raman active modes so the symmetry likely is to be C_{2h} and not C_{2v}. The latter is less likely on stereochemical grounds as repulsion between the bulky ligands would occur.

In the complexes reported here, the coordination with such Schiff base ligands, tridentate or bidentate, requires non-coplanarity of the ligand molecules. The phenyl rings are nearly perpendicular to each other as proposed earlier [19] for the free ligand. Moreover, the anion groups, NCS$^-$, NO$_3$$^-$ and Cl$^-$ require weak interaction of the two rings of Schiff base and in effect, this non-coplanarity of the ligand allows a maximum coordination number of 8 when X = OH. In addition, the C=N stretching frequency was found to be independent of the substituting group X. Such an effect, however, requires the coplanarity of the benzene ring with the C=N group.

References

1 K. C. Dash and H. N. Mohanta, *Transition Met. Chem., 2* (1977) 229.
2 R. J. Hill and C. E. F. Rickard, *J. Inorg. Nucl. Chem., 40* (1978) 793.
3 W. I. Azeez and A. I. Abdulla, *Inorg. Chim. Acta, 15* (1985) 110.
4 U. Casellato, S. Sitran, S. Tamburini, P. A. Vigato and R. Graziani, *J. Less-Common Met., 122* (1986) 257.
5 A. O. Baglaf, M. M. Aly and N. S. Ganji, *Polyhedron, 6* (1987) 205.
6 H. D. S. Yadava, S. K. Sengupta and S. C. Tripathi, *Inorg. Chim. Acta, 128* (1987) 1.
7 R. Roy, M. C. Saha and P. S. Roy, *Inorg. Chim. Acta, 129* (1987) 265.

8 B. Kuncheria and P. Indrasenan, *Polyhedron, 7* (1988) 143.

9 B. Kuncheria, G. Sobhana Devi and P. Indrasenan, *Inorg. Chim. Acta, 155* (1989) 255.

10 H. Mohanta and K. C. Dash, *J. Indian Chem. Soc., 54* (1977) 166.

11 H. Mohanta and K. C. Dash, *J. Indian Chem. Soc., 57* (1980) 26.

12 H. Mohanta and K. C. Dash, *J. Inorg. Nucl. Chem., 39* (1977) 1345.

13 A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis,* Longmans, London, 1961, pp. 540–41.

14 W. J. Chary, *Coord. Chem. Rev., 1* (1971) 81.

15 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds,* Wiley, New York, 1966.

16 D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc., 78* (1956) 1137.

17 M. Vidali, P. A. Vigato, G. Bandoli, D. A. Clemente and V. Casellato, *Inorg. Chim. Acta, 6* (1972) 671.

18 M. Choca and J. R. Ferato, *J. Chem. Soc., Dalton Trans.,* (1972) 2297.

19 M. Ahsraf El-Bayoumi, M. El-Asser and F. Abdel-Halim, *J. Am. Chem. Soc., 93* (1971) 586.