

COORDINATION CHEMISTRY OF Zr(IV), Th(IV) AND U(VI) IONS CONTAINING 1,2 DIAMINOCYCLOHEXANE N N N' N' TETRA-ACETIC ACID (DCTA) AND SOME MONODENTATE ORGANIC LIGANDS

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(Received August 15, 1994; revised October 16, 1995)

Some new mixed ligand complexes of zirconium (IV) containing 1,2 diaminocyclohexane N N N' N' tetra-acetic acid (DCTA) and some monodentate organic ligands have been synthesized and characterized. Complexes of thorium (IV) and uranium (VI) containing DCTA only have also been reported here. DCTA behaves as a hexadentate, quadrinegative ligand in all the zirconium, thorium and uranium complexes. Zirconium and uranium complexes are presumably seven and eight-coordinated respectively whereas thorium complex is octahedral. The complexes have the compositions: $[Zr(DCTA)L].nH_2O$ (where $n=1, 2$ and 3 ; L = pyridine-1-oxide, triphenylphosphine oxide (Ph_3PO), triphenylarsine oxide (Ph_3AsO), pyridine and aniline), $[Th(DCTA)].2H_2O$ and $H_2[UO_2(DCTA)].H_2O$.

Key words: Coordination chemistry, DCTA, Zr(IV), Th(IV), U(VI).

Introduction

1,2 diaminocyclohexane N N N' N' tetra-acetic acid (DCTA) is a unique polydentate quadrinegative chelating agent having analytical, therapeutic and microbiological importance [1-9]. Quadeer *et al.* [1] have reported the effect of this chelate on the yield of riboflavine formation. Reinhard *et al.* [2] have studied the stabilizing effect of DCTA on degradation of penicillamine hydrochloride. Various aminopoly carboxylic acids including DCTA have been reported [3] to assist the photoreduction of iodine in aqueous solution. Reports are available [4] on the kinetics of ligand substitution reactions of nitrilotriacetato nickel (II) complexes with trans-1, 2, cyclohexane diaminotetra acetic acid ions. Ternary chelates of niobium (V) with aminopolycarboxylic acid and polyphenols in aqueous solution have been reported [5] as reagents for niobium and tantalum. Werke [6] has applied prussian blue complexes of different polyamino acetic acids including DCTA itself with sodium chloride for deicing of roads in cold countries. Certain chelating compounds like polyaminocarboxylic acid are reported [7] to be used in photographic emulsions to prevent the desensitizing and white spot effects of metal and metal oxides. More importantly, the polyamino acetic acids have microbiological importance. Noester *et al.* [8] reported a microbiological detergent that contained 1,4 diaminocyclohexane diacetate in combination with other species like water, sodium nitrilotriacetic acid etc. Whitfield *et al.* [9] have used DCTA for complexometric determination of calcium and magnesium in the presence of sodium. Using DCTA as complexing agent Pedro [10] has developed a method for separation of mixtures of alkaline earth elements.

Knowing the importance of DCTA in microbiology and analytical chemistry we were interested to extend our studies on its coordination chemistry, mixed ligand complexes, in particular. We thus undertook a programme of synthesizing mixed ligand complexes of DCTA of Zr(IV), Th(IV) and U(VI) containing some monodentate co-ligands. We report herein the syntheses, bonding and structure of these complexes.

Experimental

Reagents. All chemicals used were reagent grade, and supplied by Merck and BDH.

Physical measurements and elemental analysis. IR spectra (as KBr discs) were recorded on a Pye Unicam SP3 300 infrared spectrophotometer and electronic spectra (as nuzol mull) on a Shimadzu UV-160 UV-visible spectrophotometer. Conductivities of 10^{-3} M solutions were measured at room temperature in dimethylsulphoxide (DMSO) using a digital conductometer CG 857 Scotte Geratte and a dip type cell with platinized electrodes. Magnetic susceptibility measurements were carried out on a Sherwood Scientific Ltd. digital magnetic susceptibility balance at $30^\circ C$.

Microanalyses for C, H and N were obtained from the microanalytical services at Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow, India.

Preparation of the Complexes: General method of preparation of $[Zr(DCTA)(L)].nH_2O$ ($n=1, 2$ and 3 ; DCTA = 1,2 diaminocyclohexane N N N' N' tetra-acetic acid and L =pyridine 1-oxide (PyO) (1), triphenylphosphine oxide (Ph_3PO) (2), triphenylarsine oxide (Ph_3AsO) (3), aniline (4) and pyridine (Py) (5)]. Equimolar quantities (0.001 mol or

0.002 mol)) of each of zirconium (IV) nitrate, hexahydrate, $Zr(NO_3)_4 \cdot 6H_2O$ and DCTA were dissolved separately in 40 cm^3 and 100 cm^3 hot methanol respectively and mixed together to get a clear solution. To this clear mixture a solution of L (0.001 mol or 0.002 mol) in methanol (10 -20 cm^3) was added and heated for 0.25 - 0.5 h at $\sim 70^\circ C$ with stirring when complex 1 -3 appeared as white solid product but complex 4 and 5 resulted as curdy white solid instantaneously at room temperature. The product was then separated, washed with methanol and ether and finally stored *in vacuo* over fused $CaCl_2$. Yields : complex 1 - 5 : 0.12 g, 0.15 g, 0.15 g, 0.25 g and 0.28 g respectively.

General method of preparation of [Th(DCTA)].2H₂O (6) and H₂[UO₂(DCTA)].H₂O (7). To the solution of thorium nitrate, pentahydrate, $Th(NO_3)_4 \cdot 5H_2O$ (0.001 mol) or uranyl nitrate, hexahydrate, $UO_2(NO_3)_2 \cdot 6H_2O$ (0.001 mol) in methanol (20-25 cm^3) a solution of DCTA (0.001 mol) in hot methanol (60-75 cm^3) was added at room temperature when complex 6 appeared as a white solid product on stirring for 5 minutes whereas complex 7 resulted instantaneously as a pale

yellow solid without stirring. It was then filtered, washed thoroughly with methanol then with ether and finally stored *In vacuo* over P_4O_{10} . Yields: complex 6: 0.56 g and complex 7: 0.45 g.

Results and Discussion

The analytical data alongwith other physical properties of the complexes are presented in Table 1. The complexes have been formulated on the basis of these analytical data and their structures proposed by the conductivity and magnetic measurements and infrared and electronic spectral studies. All the complexes except 2 and 6 were insoluble in all common organic solvents. Thus conductivity measurements could not be obtained for these insoluble complexes. Complexes 2 and 6 were found to be nonelectrolytes in DMSO [11]. This clearly indicates that the chelate anions are covalently bonded in all the complexes. Zirconium and uranium complexes are presumably seven and eight fold coordinated respectively whereas thorium complex is octahedral.

TABLE 1. ANALYTICAL DATA AND SOME PHYSICAL PROPERTIES OF THE COMPLEXES (CALCULATED VALUES ARE IN THE PARENTHESIS).

No.	Compound	Colour	Melting point ($^\circ C$)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Molar conductivity $\Omega^{-1}cm^2mol^{-1}$
1.	$[Zr(DCTA)(PyO)].2H_2O$	Colourless	270-290 (d)	40.19 (40.41)	4.28 (4.79)	7.34 (7.44)	
2.	$[Zr(DCTA)(Ph_3PO)].3H_2O$	Colourless	160-180 (d)	50.20 (50.18)	4.80 (5.10)	3.45 (3.66)	7.3
3.	$[Zr(DCTA)(Ph_3AsO)].H_2O$	Colourless	140-160 (d)	49.30 (49.67)	4.40 (4.53)	3.75 (3.62)	
4.	$[Zr(DCTA)(C_6H_5NH_2)].2H_2O$	Colourless	230-240 (d)	42.42 (42.69)	4.72 (5.16)	7.32 (7.47)	
5.	$[Zr(DCTA)(C_5H_5N)].H_2O$	Colourless	210-230 (d)	42.93 (43.00)	4.78 (4.72)	7.37 (7.92)	
6.	$[Th(DCTA)].2H_2O$	Colourless	250-275 (d)	27.38 (27.54)	3.32 (3.61)	4.42 (4.59)	9.2
7.	$H_2[UO_2(DCTA)].H_2O$	Pale yellow	190-240 (d)	26.43 (26.58)	3.05 (3.48)	4.37 (4.43)	

DCTA = 1,2 diaminocyclohexane N N N' N' tetraacetic acid. PyO = Pyridine 1-oxide, Ph_3PO = Triphenylphosphine oxide, Ph_3AsO = Triphenylarsine oxide. d = means decomposition.

TABLE 2. INFRARED SPECTRA OF THE COMPLEXES (BAND MAXIMA, cm^{-1}).

No.	$\nu(HN_2)$	$\nu(C=O)$	$\nu(C-O)$	$\nu(C=N)$	$\nu(N=O)$	$\nu(P=O)$	$\nu(As=O)$	$\nu(M-O)$	$\nu(M-N)$	$\nu(U=O)$
1.	-	1660 s	1380 m	-	1205 s	-	-	365m	300 m	-
2.	-	1660 s	1380 m	-	-	1120 s	-	445m	280 s	-
3.	-	1678 s	13880 vs	1560 s	-	-	860 s	410s	300 s	-
4.	2920 vs 2860 m	1640 s	1380 s	-	-	-	-	-	290 m	-
5.	-	1640 s	1380 vs	-	-	-	-	-	290 m	-
6.	-	1660 s	1380 s	-	-	-	-	-	358 s	-
7.	-	1650 vs	1390 s	-	-	-	-	-	380 m	920 vs

Relative band intensities are denoted by vs, s and m representing very strong, strong and medium respectively.

Infrared spectra of the complexes are displayed in Table 2. Free acetate ions in 1,2 diaminocyclohexane N N N' N' tetra-acetic acid ligand (DCTA) show bands at 1560 cm⁻¹ and 1420 cm⁻¹ corresponding to asymmetric and symmetric modes of $\nu(\text{COO}^-)$. Complexes 1-7 exhibit $\nu(\text{C=O})$ (1640-1660 cm⁻¹) and $\nu(\text{C-O})$ (~1380 cm⁻¹) modes characteristic of unidentate carboxylate binding by the DCTA in these complexes [12]. The disappearance of $\nu(\text{OH})$ band observed at 3557 cm⁻¹ for free DCTA in all the complexes is consistent with our above findings. The coordinations of pyridine-1-oxide, triphenyl phosphine oxide and triphenylarsine oxide to zirconium through oxygen in 1,2 and 3 are evident from the appearance of $\nu(\text{N=O})$, $\nu(\text{P=O})$ and $\nu(\text{As=O})$ modes at 1205 cm⁻¹, 1120 cm⁻¹ and 860 cm⁻¹ respectively [13]. These bands appear at 37 cm⁻¹, 73 cm⁻¹ and 20 cm⁻¹ respectively lower than the corresponding ligand values. This is further supported by the appearance of $\nu(\text{MO})$ stretching modes at 365-445 cm⁻¹ in the far IR region of the spectra of the complexes [14]. In 5, the appearance of $\nu(\text{C=N})$ mode at 1560 cm⁻¹ indicates that the ring nitrogen of pyridine is coordinated to zirconium [15]. Besides, the coordination of pyridine to the metal through ring nitrogen is indicated by the upward shifts of in-plane and out-of-plane deformation bands which appeared at 650 cm⁻¹ and 450 cm⁻¹ respectively [16] (corresponding free ligand values are 604 cm⁻¹ and 405 cm⁻¹ respectively). Bands appearing at 2920 cm⁻¹ and 2860 cm⁻¹ corresponding to anti-symmetric and symmetric $\nu(\text{NH}_2)$ stretching modes for the complex 4 undergo considerable downward shifts compared to the free ligand values (3080 and 3000 cm⁻¹ respectively). This clearly reveals the coordination of amino nitrogen to zirconium. This is further supported by the appearance of $\nu(\text{MN})$ modes at 290 cm⁻¹ in the far IR region of spectra of complexes [17]. Complex 7 exhibits diagnostic $\nu(\text{U=O})$ band at 920 cm⁻¹ [18,19]. The appearance of $\nu(\text{MN})$ modes at 280-380 cm⁻¹ for 1-7 suggests the imino nitrogen coordination to zirconium, thorium and uranium, thus behaving DCTA as a hexadentate, quadrinegative ligand. All complexes show bands at ~3400 cm⁻¹ corresponding to lattice water molecules. Attempts to prepare mixed ligand complexes of thorium and uranium using DCTA and other monodentate co-ligands were unsuccessful. However, DCTA itself combines with Th(IV) and U(VI) giving these precipitates leaving no room for coordination with the type of monodentate co-ligands used for zirconium. The instantaneous precipitation of thorium and uranium with DCTA can be attributed to their large atomic size giving presumably a better crystal packing compared to the case of zirconium which is decidedly smaller in size.

The complexes 1-7 were all diamagnetic giving negative molar susceptibilities consistent with the vacant d orbital character of metal ions. The electronic spectral bands of the com-

TABLE 3. CHARGE TRANSFER BANDS OF THE COMPLEXES (BAND MAXIMA, nm).

Complex	Band I	Band II	Band III
1	380	306	244
2	370	306	241
3	360	305	234
4	344	306	241
5	344	306	242
6	347	300	238
7	342	-	243

plexes, 1-7 are shown in Table 3. Since the metal ions are d systems, they are not supposed to produce d-d transition bands. Obviously the bands shown here are caused by ligand to metal charge transfer (LMCT). Brisdon *et al.* [20] have shown that six-coordinated halide complexes of Zr(IV) exhibit one LMCT at ~238 nm. But each of the present Zr(IV) complexes 1-5 exhibit three LMCT bands in the ultraviolet region *viz.*, 344-380 nm, ~305 nm and 234-244 nm probably corresponding to the transitions, $\pi 1t_{2g} - 2t_{2g}$, $(\pi+\sigma) 2t_{1u} - 2t_{2g}$ and $(\pi+\sigma) 2t_{1u} - 2e_g$ respectively [21]. These transitions have been identified with those of Nb(V), because both Zr(IV) and Nb(V) are d systems and belong to the same transition series. The little oxidising behaviour of Zr(IV) [22] towards the ligand DCTA plays a vital role in determining the position of LMCT bands. Again the position and number of charge transfer bands are dependent on the donor capacity of ligand and on geometry of the complexes [22]. Th(IV) and U(VI) complexes also exhibit three (344 nm, 306 nm and 238 nm) and two (342 nm and 243 nm) LMCT bands respectively (Table 3). The production of LMCT bands in the wide range of ultraviolet region is rationalised in terms of mixed covalent and ionic characters of the ligand to metal bonding in all complexes. Exact assignment of transition to bands of Th(IV) and U(VI) complexes was not possible due to lack of related information, but they might be correlated with the transitions mentioned for Zr(IV), owing to the fact that metal ions belong to the same group.

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