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PREPARATION AND REACTIVITY OF SOME PEROXO COMPLEXES OF ZIRCONIUM(IV) AND URANIUM(VI)

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ABSTRACT

New peroxo complexes of zirconium(IV) and uranium(IV) with dibasic acids and nitrogen containing heterocyclic bases have been prepared. The general compositions of the complexes are $[M(O_2)(DB)(L)_2]$ and $[M'O(O_2)(DB)(L)_2]$, where M, M′ are Zr(IV) or U(VI), DB = dianion of homophthalic acid or malonic acid and L = quinoline (Q) or isoquinoline (IQ). These complexes were characterized on the basis of elemental analyses, conductivity measurements, magnetic measurements, TLC, GLC, infrared spectral studies and by reactions with allyl alcohol, triphenylphosphine and triphenylarsine. The zirconium complexes were found to be octahedral, whereas the uranium complexes were seven-coordinated.

INTRODUCTION

Studies on peroxo complexes have received considerable encouragement in recent years due to their application as oxidants in synthetic organic chemistry[1-10]. Many of the peroxo complexes are the source of active oxygen atoms and can be used as catalysts of oxygen insertion reactions and as oxidants for organic and inorganic substrates[6-13]. Peroxo complexes have recently been shown to be active species in the copper catalyzed oxidation of alcohol to ketone and oxidative cleavage of pyrocatechol[8].

Keeping this fact in mind, we have submitted herein the synthesis and properties (viz. oxygen transfer reaction to various substrates) of some newer peroxo complexes of Zr(IV) and U(VI) with amine bases [quinoline (Q) and isoquinoline(IQ)] and dibasic acids [homophthalic acid (Pth) and malonic acid(Mal)]. The structure and properties of these complexes were analysed with the help of elemental analyses, magnetic moment, conductivity, TLC, GLC and IR spectral studies.

RESULTS AND DISCUSSION

The complexes are formed by the following steps:

$$Zr(NO_3)_4 + 2L + DBH_2 + H_2O_2 \longrightarrow [Zr(O_2)(DB)(L)_2] + 4HNO_3$$

$$UO_2(NO_3)_2 + 2L + DBH_2 + H_2O_2 \longrightarrow [UO(O_2)DB)(L)_2] + 2HNO_3 + H_2O$$

Where DBH_2 = homophthalic acid or malonic acid and L = quinoline (Q) or isoquinoline (IQ).

Conductivity

The analytical data and other physical properties of these complexes are given in Table I. All of the complexes are insoluble in water but soluble in DMF, DMSO and nitrobenzene. The molar conductance values of these complexes in DMSO indicate their non-electrolytic behaviour and further reveal the covalent bond between the anion and the metal atoms.

IR Studies

IR spectral data are shown in Table II. The complexes showed absorptions for ν(C=O) bands at 1600-1630 cm^{-1} in comparison with the free acid carbonyl group at 1700 cm^{-1}. This reduction of frequency is indicating the linkage between metal and oxygen atom. Again, distinct IR absorption at 430-471 cm^{-1} indicates metal oxygen bond formation[14]. In these complexes C-O stretching modes of vibration occur at 1381-1411 cm^{-1} indicating the coordination between metal and oxygen atoms[15]. The

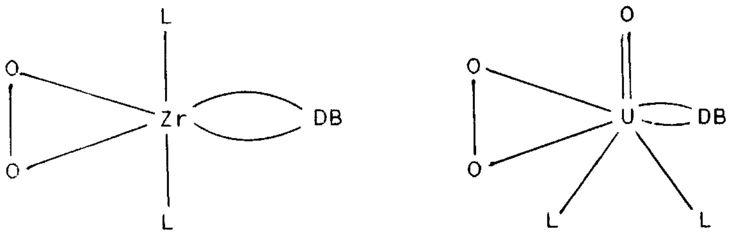

Fig. 1. General Skeletal Structures of the Complexes
L = Q or IQ; DB = Pth or Mal.

appearance of the absorption at 360-340 cm^{-1} indicates a metal nitrogen bond[16]. The metal peroxo grouping gives rise to three IR active vibrational modes. These are chiefly due to ν(O-O), ν_{asm}(M-O-O) and ν_s(M-O-O). These characteristic vibration modes for complexes (1)-(4) appear at 825-845 cm^{-1} and for the complexes (5)-(8) at 805-820 cm^{-1}, respectively. Thus, this study confirmed the M(O_2) grouping and suggests that ν(O-O) modes of vibration decrease with the increasing atomic number of metal atoms[17]. In these complexes, the ν_{asm}(M-O-O) and ν_s(M-O-O) modes of vibration appear at 664-688 cm^{-1} and 595-622 cm^{-1}, respectively. Another important absorption occurs at 910-945 cm^{-1} for the complexes (5)-(8) indicating a distinct M=O mode of vibration of those complexes. For the Zr complexes ν(M=O) vibrations are absent.

From the above discussion the general skeletal stuctures of the complexes can be proposed as the following (Fig. 1).

Table I. Analytical and Physical Data of the Complexes.

Compound[a]	Molecular weight (Formula weight)	Decomp. point (± 0.5 °C)	Yield (%)	Metal[b] %	Carbon[b] (%)	Hydrogen[b] %	Nitrogen[b] %	Molar Conductance (ohm^{-1}cm^{2}mole^{-1})
$[Zr(O_2)(Pth)(Q)_2]$ (1) $(ZrC_{26}H_{18}O_6N_2)$	535.10 (545.22)	250 (d)	67	16.73 (16.51)	57.22 (57.52)	3.30 (3.00)	5.13 (5.06)	7.6
$(Zr(O_2(Pth)(IQ)_2]$ (2) $(ZrC_{26}H_{18}O_6N_2)$	538.20 (545.22)	220 (d)	66	16.73 (16.42)	57.22 (57.40)	3.30 (3.59)	5.13 (4.92)	6.4
$[Zr(O_2)(Mal)((Q)_2]$ (3) $(ZrC_{21}H_{16}O_5N_2)$	476.50 (483.22)	290 (d)	72	18.87 (19.09)	52.15 (52.00)	3.31 (3.11)	5.79 (5.99)	9.2
$[Zr(O_2)(Mal)((IQ)_2]$ (4) $(ZrC_{21}H_{16}O_6N_2)$	474.30 (483.22)	291 (d)	70	18.87 (19.00)	52.15 (51.90)	3.31 (3.42)	5.79 (5.52)	12.4
$[UO(O_2)(Pth)(Q)_2]$ (5) $(UC_{26}H_{18}O_7N_2)$	701.12 (708.03)	185 (d)	76	33.61 (33.30)	44.06 (43.92)	2.54 (2.29)	3.95 (3.71)	4.4
$[UO(O_2)(Pth)(IQ)_2]$ (6) $(UC_{26}H_{18}O_7N_2)$	704.15 (708.03)	200 (d)	72	33.61 (33.92)	44.06 (44.35)	2.54 (2.72)	3.95 (3.71)	4.9
$[UO(O_2)(Mal)(Q)_2]$ (7) $(UC_{21}H_{16}O_7N_2)$	635.27 (646.03)	190 (d)	70	36.84 (36.59)	39.00 (39.21)	2.47 (2.30)	4.33 (4.40)	8.4
$[UO(O_2)(Mal)(IQ)_2]$ (8) $(UC_{21}H_{16}O_7N_2)$	637.35 (646.03)	240 (d)	69	36.84 (37.00)	39.00 (39.25)	2.47 (2.34)	4.33 (4.25)	7.9

a $Pth^{2-} = C_8H_4O_4$, $Mal^{2-} = C_3H_2O_4$, $Q = C_9H_7N$, $IQ = C_9H_7N$,

b Experimental values are in parentheses.

IR Spectra of the Reaction Products

The peroxo complexes were found to liberate iodine within 1-2 minutes on treatment with aqueous potassium iodide. In view of this property, the possibility of reaction with olefinic compounds was explored. A stoichiometric mixture of **(2)** or **(4)** (see Table I) with allyl alcohol did not show any reaction. But compounds (5) or (8) reacted stoichiometrically with allyl alcohol forming glycidol as indicated by a separate spot in TLC and an IR band at 1050

cm^{-1} due to the C-O-C stretching mode. Compounds (5) or (8) used as a catalytic oxidative reagent with H_2O_2 for the oxidation of allyl alcohol gave glycidol as the isolated product. The IR spectrum of this product was identical with authentic sample. Reactions with triphenylphosphine or triphenylarsine formed triphenylphosphine oxide or triphenylarsine oxide showing IR absorptions at 1190 and 885 cm^{-1} due to ν(P=O) and ν(As=O) modes, respectively[18-20]. The disappearance of the ν(O-O) absorptions after the reaction in the spectra of the reacting complexes indicated the oxygen transfer to the substrate molecule.

Thus, it is seen that in complexes (5) and (8) the metal peroxo moiety is not so stabilized as to prevent the oxidation reaction with allyl alcohol, whereas in other complexes the metal peroxo moiety is greatly stabilized by the presence of mono- and bidentate organic ligands and thus preventing oxidation reactions to occur.

EXPERIMENTAL

Physical Measurements

The IR spectra were recorded on a Pye-Unicam SP3-300 infrared spectrophotometer as KBr pellets in the region 4000-600 cm^{-1} and as Nujol mulls sandwiched between CsI plates in the region 600-200 cm^{-1}. Conductivities of 1.0 x 10^{-3} mole dm^{-3} solutions of the complexes in DMSO were measured at 28°C using a WPA CM 35 conductivity meter and a dip-type cell with platinised electrodes. Decomposition points of the complexes were recorded with an electrothermal melting point apparatus. The molecular weights of the complexes were determined in nitrobenzene by the cryoscopic method. Metals were determined gravimetrically and carbon, nitrogen and hydrogen were determined by a standard literature method.

Reagents and Chemicals

All chemicals were reagent grade and obtained from E. Merck or B.D.H.

Preparation of the Complexes

The general method for the preparation of the complexes $[M(O_2)(DB)(L)_2]$ and $[M'O(O_2)DB)(L)_2]$ [where M is Zr(IV) and M'is U(VI)] was the following.

A solution of Zr(IV) nitrate hexahydrate, (0.894 g, 2 mmol) or uranyl nitrate, hexahydrate (1.04 g, 2 mmol) in distilled water (20 mL) was mixed homogeneously with an ethanolic solution (30 mL) of dibasic acid (2 mmol). A solution of quinoline (0.516 g, 4 mmol) or isoquinoline (0.516 g, 4 mmol) was made in ethanol (30 mL) and was added to the ice cooled previous mixture, followed by the simultaneous addition of 30% H_2O_2 (30 mL) solution with constant stirring for 30 minutes. Precipitation was observed and the precipitate was filtered off and successively washed with water and ethanol. Pure compounds were obtained after TLC and the products were dried in a

Table II. IR Spectral Data (Band Maxima in cm^{-1}).

Complex no.*	$\nu_{C=O}$	ν_{C-O}	$\nu_{M=O}$	$\nu_{1(C-O)}$	$\nu_{asm(M<^{O}_{O})}$	$\nu_{s(M<^{O}_{O})}$	$\nu_{(M-O)}$	$\nu_{(M-N)}$
(1)	1602	1406	---	837	688	622	467	315
(2)	1600	1407	---	825	690	625	471	312
(3)	1625	1380	---	845	675	617	471	330
(4)	1630	1410	---	840	680	620	469	320
(5)	1618	1381	910	828	660	610	458	335
(6)	1620	1400	920	825	635	621	465	337
(7)	1622	1411	940	820	671	595	450	360
(8)	1626	1415	945	825	664	600	430	355

*Please see Table I.

vacuum desiccator over silica gel. The zirconium complexes were white to off-white whereas the uranium complexes were yellow to yellowish.

Reactions of (2) and (4) with Allyl Alcohol

The compound (2) (0.272 g, 0.5 mmol) (see Table I) was suspended in 10 mL tetrahydrofuran (THF) and a stoichiometric amount (0.029 g, 0.5 mmol) of allyl alcohol was added. The mixture was stirred under reflux at 60°C for 48 h but failed to produce any reaction product and **(2)** was recovered unchanged. Compound **(4)** also failed to give any reaction product.

Reactions of (5) and (8) with Allyl Alcohol

A stoichiometric amount (0.029 g, 0.5 mmol) of allyl alcohol was added to a suspension of compound (5) (0.272 g, 0.5 mmol) in THF (10 mL). The mixture was stirred under reflux at 60°C for 36 h. Microdistillation at 19 mm of Hg yielded glycidol (0.306 g, 69%) bp 147-150°C [IR (Nujol) 1055 cm^{-1} (S, C-O-C)]. The glycidol was firmly identified by preparing its phenylurethane derivative, mp 58-59°C (lit.[22] mp 60°C). Compound (8) behaved in a similar fashion.

Reactions of (3),(5) and (8) with Triphenylphosphine

A solution of triphenylphosphine (0.131 g, 0.5 mmol) in THF (10 mL) was added to a suspension of complex

(8) (0.328 g, 0.5 mmol) in THF (20 mL). The mixture was stirred under reflux for 36 h in all cases. The progress of the reaction was monitored by TLC which showed formation of the product. The product was a yellowish white powder and was identified as triphenylphosphine oxide (mp 156-157 °C) by mixed melting point with an authentic sample (lit.[21] mp 157°C). Compound (3) and (5) behaved in a similar fashion.

Reactions of (1),(6),(7) with Triphenylarsine

A solution of triphenylarsine (0.153 g, 0.5 mmol) in THF (15 mL) was added to a suspension of compound (7) (0.323 g, 0.5 mmol) in THF (30 mL). The mixture was refluxed for about 24 h and subjected to TLC indicating completion of the reaction. The reaction mixture was then filtered and residue was collected. After treatment by column chromatography pure triphenylarsine was obtained, mp 188-189°C (lit.[18] mp 190-192 °C).

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