

## Short Communication

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### Complexes of Zr(IV) and U(VI) with Trans- [14]-diene

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Some new complexes of zirconium (IV) and uranium (VI) containing a tetraazamacrocycle and other organic ligands have been synthesized and characterized. The complexes have composition,  $[Zr(L).2L'] (NO_3)_4$ ,  $[Zr(L).en] (NO_3)_4$  and  $[U(O)_2 (L).L'] (NO_3)_2$ ;  $[L=trans-(14)-diene; en=ethylenediamine; L' = pyridine (Py), triphenylphosphine oxide (OPPh_3) or triphenylarsine oxide (OAsPh_3)]$ .

Transition metal complexes with macrocyclic ligands are important for their distinctive coordination chemistry and biological significance [1-5]; but macrocyclic complexes of heavier metal ions are lacking so. The synthesis and characterization of some complexes of Zr(IV) and U(VI) with trans (14)-diene containing Py, en, OPPh<sub>3</sub> and OAsPh<sub>3</sub> as auxiliary ligands are reported here.

Reagent grade chemicals of (Merck) were used. Ethanol was purified as reported earlier [6]. Trans. (14)-diene (C<sub>16</sub>H<sub>32</sub>N<sub>4</sub>) as its dihydrobromidedihydrate salt of the structure as shown in Fig. 1 was prepared following a method reported in the literature [7].

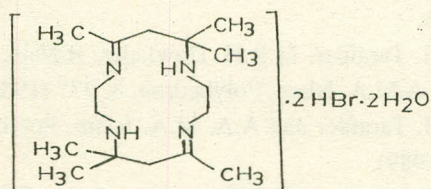


Fig. 1. L.2HBr. 2H<sub>2</sub>O

Complexes 1,3 and 4,  $[Zr(L).2L'] (NO_3)_4$   $[L=C_{16}H_{32}N_4; L'=Py, OPPh_3 \text{ or } OAsPh_3]$ . To the solution of  $Zr(NO_3)_4 \cdot 6H_2O$  (0.002 mol) in water (30 cm<sup>3</sup>) was added to the solution of L.2HBr. 2H<sub>2</sub>O (0.002 mol) in absolute ethanol (60 cm<sup>3</sup>) followed by the addition of L' (0.004 mol) in absolute ethanol (20 cm<sup>3</sup>). The complexes formed instantaneously were separated and washed successively with water and ether and finally dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>.

Complexes 2,  $[Zr(L).en] (NO_3)_4$   $[L=C_{16}H_{32}N_4; en=ethylenediamine]$ . A solution of  $Zr(NO_3)_4 \cdot 6H_2O$  (0.002 mol) in water (40 cm<sup>3</sup>) was added to a solution of L.2HBr. 2H<sub>2</sub>O (0.002 mol) in absolute ethanol (60 cm<sup>3</sup>) and treated with a solution of ethylenediamine (0.002 mol) in absolute

ethanol (30 cm<sup>3</sup>). The white product obtained was filtered, washed and stored as above.

Complexes 5 and 6,  $[U(O)_2 (L).L'] (NO_3)_2$   $[L=C_{16}H_{32}N_4; L'=Py \text{ or } OPPh_3]$ . A solution of  $U(O)_2 (NO_3)_2 \cdot 6H_2O$  (0.002 mol) in absolute ethanol (20 cm<sup>3</sup>) was added to a solution of L.2HBr. 2H<sub>2</sub>O (0.002 mol) in the same solvent (60 cm<sup>3</sup>). A solution of L' (0.002 mol) in absolute ethanol (15 cm<sup>3</sup>) was then added to the above mixture. The mixture was heated on water bath at 45°C for 5 min.. After cooling for some time a yellow product was obtained which was separated and stored as above.

IR spectra (as KBr discs) were recorded on a Pye-Unicam SP3-300 infrared spectrophotometer. Conductivities of 10<sup>-3</sup> mol dm<sup>-3</sup> solutions of the complexes were measured at ~25°C in dimethylsulfoxide (DMSO) using a dip-cell with platinumized electrodes and a PTI-18 digital conductivity meter.

The analytical and conductivity data and the infrared spectral data are given in Tables 1 and 2 respectively. The experimental data are consistent with six fold coordination of Zr(IV) while U(VI) ions are seven fold coordinated. Complexes 1-4 are 4:1 while 5 and 6 are 2:1 electrolytes in DMSO.

In the IR spectra of the complexes, the  $\nu$  (NH) and  $\nu$  (C=N) bands of the free ligand are shifted to lower frequencies indicating coordination of the macrocycle through its N atoms; the bands found at ~1380, ~810 and ~720 cm<sup>-1</sup> are due to ionic nitrates [8,9] outside the coordination spheres. Again, lower  $\nu$  (C=N),  $\nu$  (P=O) and  $\nu$  (As=O) values than the corresponding free auxiliary ligand values of 1610 cm<sup>-1</sup> [10-14,19], 1192 cm<sup>-1</sup> [15] and 880 cm<sup>-1</sup> [16] together with the observed  $\nu$  (M-N) and  $\nu$  (M=O) modes suggest coordination through N of Pyridine and O of OPPh<sub>3</sub> and OAsPh<sub>3</sub> [17-20]. Complex 2 shows  $\nu$  (NH<sub>2</sub>) bands at 3360 and 2920 cm<sup>-1</sup> while 5 and 6 display  $\nu$  (U=O) modes [17,21,22] at 920 and 930 cm<sup>-1</sup>. Zr (IV) complexes were assumed to have octahedral but  $\nu$  (VI) is a distorted pentagonal bipyramidal structure [23]; the latter are coloured due to  $\nu$  to  $\nu$  transition [23].

**Key words:** Heavy metals, Complexes, Macrocyclic ligand.

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TABLE 1. ANALYTICAL DATA AND OTHER PHYSICAL PROPERTIES OF THE COMPLEXES.

Compound	No	Colour	Calc. (Found) %			Conductance $\Omega^{-1}\text{cm}^2 \text{mol}^{-1}$
			C	H	N	
[Zr(L).2Py](NO <sub>3</sub> ) <sub>4</sub>	1	White	40.15(40.01)	5.44(5.43)	18.01(18.00)	118
[Zr(L).en](NO <sub>3</sub> ) <sub>4</sub>	2	-do-	31.80(31.65)	5.93(5.65)	20.61(20.43)	121
[Zr(L).20PPh <sub>3</sub> ](NO <sub>3</sub> ) <sub>4</sub>	3	-do-	53.09(53.00)	5.31(5.25)	9.53(9.41)	130
[Zr(L)20AsPh <sub>3</sub> ](NO <sub>3</sub> ) <sub>4</sub>	4	-do-	49.41(49.31)	4.94(4.75)	8.86(8.59)	125
[U(O <sub>2</sub> )(L).Py](NO <sub>3</sub> ) <sub>2</sub>	5	Yellow	33.47(33.41)	4.95(4.82)	13.01(13.00)	63
[U(O <sub>2</sub> )(L)OPPh <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	6	-do-	42.86(42.65)	4.97(4.77)	8.82(8.75)	60

L=trans-[14]-diene (C<sub>16</sub>H<sub>32</sub>N<sub>4</sub>).

TABLE 2. IR( $\nu$  max in cm<sup>-1</sup>) SPECTRAL DATA OF THE LIGAND AND COMPLEXES.\*

Com- pound*	$\nu$ (N-H)	$\nu$ (C=N)	$\nu$ (P=O)	$\nu$ (M-O)	$\nu$ (M-N)	Other bands
L	3460s	1660s				
1	3380m	1585m			370sh	1375s,830w,710sh
2	3360br	1620m			32ow	1375s,825w,710sh
3	3380m	1610m	860m	470m	350w	1370s,805w,710m
4	3380br	1610m	1110m	520w	380w	1375s,815w,730m
5	3400br	1585m			320w	1380s,820m,710sh,920s
6	3410m	1580s	1125vs	455m	325w	1375s,800m,720s,930s.

\*The band intensities are denoted by vs, s, m, w, br and sh meaning very strong, strong, medium, weak, broad and shoulder respectively. +See Table 1

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