

## MIXED LIGAND COMPLEXES INCLUDING COMPLEXES OF TETRAAZAMACROCYCLES

M.T.H. TARAFDER, A.H.M.M. ZAHAN, P. BHATTACHARJEE, S.C. PAL AND M.N. UDDIN\*  
*Department of Chemistry, Rajshahi University, Rajshahi - 6205, Bangladesh*

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Several new mixed ligand complexes of zirconium (IV), uranium (VI), copper (II) and zinc (II) of compositions,  $[Zr(O)Cl_2L'L'']$  [ $L'$ =*o*-phenylenediamine, ethylenediamine, 1,6-diaminohexane and  $L''$ =quinoline, pyridine pyridine N-oxide and aniline];  $[Zr(O)Cl_22L'L'']$  [ $L'$ =aniline and  $L''$ =pyridine N-oxide];  $[Zr(O)[14]ane N_4Cl]Cl$ ;  $[U(O)_2[14]ane N_4](NO_3)_2$  and  $[ML]X_2$  [ $M$ =Cu(II) and Zr(II),  $L$ =trans-[14]-diene and  $X$ =Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>] have been synthesized and characterized. Conductivity measurements reveal that complex 1 is nonelectrolyte and copper (II) and zinc (II) complexes are 2:1 electrolytes in DMSO. But such measurements could not be carried out for other complexes due to their insolubility in almost all common organic solvents. Magnetic measurements, IR and electronic spectral data are consistent with octahedral geometry of zirconium (IV) and uranium (VI) complexes and four-coordinated square planar geometry of copper (II) and zinc (II) complexes.

**Key words.** Metal complexes, Tetraazamacrocycles, Mixed ligands.

### Introduction

Mixed ligand complexes of different metals containing nitrogen and oxygen donors are well-known to serve pharmaceutical [1-3] and industrial interests [4-7]. Transition metal complexes of phthalimide have therapeutic [8,9] and industrial importance [10,12]. Sharma *et al.* [13] have reported a number of mixed ligand complexes of titanium (III) and vanadium (IV) with imides and heterocyclic bases. They have also reported [14] mixed ligand complexes of cobalt (II) and nickel (II) containing diphenic acid as a primary and heterocyclic bases as secondary ligands. Complexes with macrocyclic ligand have received considerable attention, since they exhibit distinctive coordination chemistry and biological activity [14-19]. Hay *et al.* [20,21] have reported a number of cis-complexes of macrocyclic ligands. Considering these facts a study was conducted and mixed ligand complexes of heavier metals, Zr(IV) and U(VI) ions and metal complexes of Cu(II) and Zn(II) ions containing 14 and 15-membered macrocycles and their syntheses, bonding and structures are reported.

### Experimental

**Reagents and chemicals.** All reagents and chemicals were of reagent grade and used as supplied by E. Merck, except for ethanol which was refluxed with iodine and magnesium turnings, distilled and stored over molecular sieves.

**Analyses.** Carbon, hydrogen and nitrogen analyses were carried out by the microanalytical services at the University of Erlangen - Nurnberg, Germany.

**Preparation of the Complexes: Preparation of (1):**  $[Zr(O)Cl_2.C_6H_4(NH_2)_2.C_9H_7N]$ .  $ZrOCl_2.8H_2O$  (0.5 g, 0.0025 mol) was dissolved in absolute ethanol (30 cm<sup>3</sup>) to which an ethanolic solution (40 cm<sup>3</sup>) of *o*-phenylenediamine (0.27g, 0.0025 mol) and quinoline (0.33 g, 0.0025 mol) was added. The precipitate was filtered, washed with absolute ethanol and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub> to get coffee coloured solid (yield 60%).

**Preparation of (2):**  $[Zr(O)Cl_2.2C_6H_5(NH_2).C_5H_5NO]$ .  $ZrOCl_2.8H_2O$  (0.5g, 0.0025 mol) was dissolved in absolute ethanol (30 cm<sup>3</sup>) to which an ethanolic solution (40 cm<sup>3</sup>) of aniline (0.46 g, 0.050 mol) and pyridine N-oxide (0.24g, 0.0025 mol) was added. The blue solid was filtered, washed with absolute ethanol and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub> (yield 65%).

**Preparation of (3):**  $[Zr(O)Cl_2(en).C_6H_5NH_2]$ .  $ZrOCl_2.8H_2O$  (0.5 g, 0.0025 mol) was dissolved in absolute ethanol (30 cm<sup>3</sup>) to which an ethanolic solution of ethylenediamine (0.15g, 0.0025 mol) and aniline (0.23 g, 0.0025 mol) was added. The precipitate was isolated, washed with absolute ethanol and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub> to get yellowish solid (yield 70%).

**Preparation of (4):**  $[Zr(O)Cl_2.NH_2(CH_2)_6NH_2.C_6H_5NH_2]$ .  $ZrOCl_2.8H_2O$  (0.5g, 0.0025 mol) was dissolved in absolute ethanol (30 cm<sup>3</sup>) to which an ethanolic solution (40 cm<sup>3</sup>) of 1,6-diaminohexane (0.29 g, 0.0025 mol) and aniline (0.23 g, 0.0025 mol) was added. The precipitate was filtered, washed with absolute ethanol and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub> to get grey solid (yield 62%).

**Preparation of (5):**  $[Zr(O)Cl_2.NH_2(CH_2)_6NH_2.C_9H_7N]$ .  $ZrOCl_2.8H_2O$  (0.5g, 0.0025 mol) was dissolved in absolute

\*Department of Chemistry, Chittagong University, Chittagong, Bangladesh.



ethanol (30 cm<sup>3</sup>) to which an ethanolic solution (40 cm<sup>3</sup>) of 1, 6-diaminohexane (0.29 g, 0.0025 mol) and quinoline (0.32 g, 0.0025 mol) was added. The grey solid was filtered, washed with absolute ethanol and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub> (yield 55%).

*Preparation of (6):* [Zr(O)Cl<sub>2</sub>.NH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>NH<sub>2</sub>.C<sub>5</sub>H<sub>5</sub>NO]. ZrOCl<sub>2</sub>.8H<sub>2</sub>O (0.5g, 0.0025 mol) was dissolved in absolute ethanol (30 cm<sup>3</sup>) to which an ethanolic solution (40 cm<sup>3</sup>) of 1,6-diaminohexane (0.29 g, 0.0025 mol) and pyridine-N-oxide (0.24 g, 0.0025 mol) was added. The precipitate was filtered, washed with absolute ethanol and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub> to get white solid (yield 58%).

*Preparation of (7):* [Zr(O)[14]ane N<sub>4</sub>Cl]Cl. A solution of ZrOCl<sub>2</sub>.8H<sub>2</sub>O (0.81g, 0.0025 mol) in absolute ethanol (40 cm<sup>3</sup>) was added to a solution of [14]ane N<sub>4</sub> (0.50 g, 0.0025 mol) in the same solvent (40 cm<sup>3</sup>). The precipitate was filtered and washed with absolute ethanol and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub> to get white solid (yield 68%).

*Preparation of (8):* [U(O)<sup>2</sup> [14]ane N<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub>. A solution of U(O)<sub>2</sub> (NO<sub>3</sub>)<sub>2</sub>. 6H<sub>2</sub>O (1.25 g, 0.0025 mol) in absolute ethanol (20 cm<sup>3</sup>) was added to a solution of [14]ane N<sub>4</sub> (0.050 g, 0.0025 mol) in the same solvent (40 cm<sup>3</sup>). The precipitate, that appeared was filtered, washed with absolute ethanol and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub> to get yellow crystals (yield 51%).

*Preparation of (9):* [Cu trans-[14]-diene] (NO<sub>3</sub>)<sub>2</sub>. A solution of Cu(NO<sub>3</sub>)<sub>2</sub>. 3H<sub>2</sub>O (0.43g, 0.0023 mol) in absolute ethanol (30 cm<sup>3</sup>) was added to a solution of trans-[14] diene (0.50 g, 0.0023 mol) in the same solvent (60 cm<sup>3</sup>). The precipitate was filtered, washed with absolute ethanol and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub> to get violet solid (yield 55%).

*Preparation of (10):* [Zn trans-[14]-diene] Cl<sub>2</sub>. A solution of ZnCl<sub>2</sub>. 6H<sub>2</sub>O (0.31g, 0.0023 mol) in absolute ethanol

(30 cm<sup>3</sup>) was added to a solution of trans- [14]- diene (0.50g, 0.0023 mol) in the same solvent (60 cm<sup>3</sup>). The precipitate, that resulted, was filtered, washed with absolute ethanol and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub> to get white solid (yield 71%).

Infrared spectra were obtained (as KBr discs) on Mattson Polaries TM Infrared Spectrophotometer (using the He-Ne Laser Class II, with a maximum output of 40 microwatts) and electronic spectra with a Shimadzu UV-vis Recording Spectrophotometer. Conductivities of 10<sup>-3</sup> M solutions of the complexes in dimethylsulphoxide (DMSO) were measured at 30°C using a digital conductometer, Scotte Geratte CG 857 and a dip type cell with plantinized electrodes.

### Results and Discussion

*Analytical data and physical properties.* The analytical data and physical properties of the complexes are presented in Table 1. The molar conductance values indicate that complex 1 is nonelectrolyte and complexes 9 and 10 are 2:1 electrolytes in DMSO [22]. The molar conductivities of all other complexes could not be measured, because they were insoluble in almost all common organic solvents.

*IR studies.* The infrared spectral data are given in Table 2. Complexes 1-6 display ν(NH<sub>2</sub>) stretching band at 3020-3320 cm<sup>-1</sup> and at 3190-3400 cm<sup>-1</sup> corresponding to symmetric and asymmetric modes significantly lower than the free ligand values (3180-3380 cm<sup>-1</sup> and 3260-3440 cm<sup>-1</sup>) indicating the coordination of amino nitrogens to the metal in these complexes. Complexes 7-10 show ν(NH) stretching band at 3040-3160 cm<sup>-1</sup> sufficiently lower than free ligand values ([14]ane N<sub>4</sub>:3280 cm<sup>-1</sup> and trans-[14] diene: 3460 cm<sup>-1</sup>) which indicate the coordination of imino nitrogens to the metals [23,24]. This is also evident from the appearance of bands at 370-440 cm<sup>-1</sup> which are attributed to ν(M-N) mode [25-27]. In com-

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

No.	Compound	Colour	% Carbon		% Hydrogen		% Nitrogen		Molar conductance Ω <sup>-1</sup> cm <sup>-1</sup> mol <sup>-1</sup>
			Calcd.	Found	Calcd.	Found	Calcd.	Found	
1	[Zr(O)Cl <sub>2</sub> .C <sub>6</sub> H <sub>4</sub> (NH <sub>2</sub> ) <sub>2</sub> .C <sub>9</sub> H <sub>7</sub> N]	Coffee	43.35	43.14	3.61	3.35	10.12	10.00	2.0
2	[Zr(O)Cl <sub>2</sub> .2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> .C <sub>5</sub> H <sub>5</sub> NO]	Blue	44.42	44.21	4.14	4.03	9.15	9.10	
3	[Zr(O)Cl <sub>2</sub> .(en).C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> ]	Light yellow	28.98	28.58	4.53	4.43	12.68	12.36	
4	[Zr(O)Cl <sub>2</sub> .NH <sub>2</sub> (CH <sub>2</sub> ) <sub>6</sub> NH <sub>2</sub> .C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> ]	Grey	37.67	37.66	4.71	4.65	10.99	10.48	
5	[Zr(O)Cl <sub>2</sub> .NH <sub>2</sub> (CH <sub>2</sub> ) <sub>6</sub> NH <sub>2</sub> .C <sub>9</sub> H <sub>7</sub> N]	Grey	42.53	42.41	5.43	5.32	9.92	9.67	
6	[Zr(O)Cl <sub>2</sub> .NH <sub>2</sub> (CH <sub>2</sub> ) <sub>6</sub> NH <sub>2</sub> .C <sub>5</sub> H <sub>5</sub> NO]	White	33.91	33.73	5.39	5.25	10.79	10.67	
7	[Zr(O)[14]ane N <sub>4</sub> Cl]Cl	White	31.73	31.66	6.35	6.31	14.81	14.59	
8	[U(O) <sub>2</sub> [14]ane N <sub>4</sub> ](NO <sub>3</sub> ) <sub>2</sub>	Yellow	20.20	20.00	4.04	4.00	14.14	13.98	
9	[Cu trans[14]-diene] (NO <sub>3</sub> ) <sub>2</sub>	Violet	41.07	41.00	6.84	6.53	11.98	11.65	57.10
10	[Zn trans [14] -diene] Cl <sub>2</sub>	White	46.11	45.77	7.68	7.52	13.45	13.22	63.20



TABLE 2. IR SPECTRAL DATA OF THE COMPLEXES (BAND MAXIMA,  $\text{cm}^{-1}$ ).

No.	$\nu(\text{NH}_2)$	$\nu(\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{N})$	$\nu(\text{M}=\text{O})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{Cl})$	Others
1	3350w 3320w		1505m	1115w	920sh		400w	300m	
2	3400w 3120w		1530m	1100w	840s	445w	405w	300m	
3	3190w 3020w			1160m	940w		400w	310w	
4	3380w 3080w			1120w	930m		405w	270m	
5	3280w 3060w		1500s	1120sh	922sh		400w	290m	
6	3380w 3050w		1530m	1170w	925m	470w	440m	300m	
7		3150m		1080sh	920m		378m	300s	
8		3040w		1118s	910s		375w		1380s, 810m, 760m.
9		3160m	1530w	1165s			370w		1365m, 830m, 750m.
10		3100s	1530s	1160m			410m		

Relative band intensities: vs= very strong, s=strong, m=medium, br= broad, w= weak and sh= shoulder.

plexes 1,2,5,6,9 and 10, the  $\nu(\text{C}=\text{N})$  [28] modes appear at 1500-1530  $\text{cm}^{-1}$  which is lower than free ligand value (1660  $\text{cm}^{-1}$ ), suggesting coordination by methine nitrogen atom. The  $\nu(\text{C}-\text{N})$  stretching modes [29] in all complexes appear at 1080-1170  $\text{cm}^{-1}$  which are lower than free ligand values. This also indicates coordination of the (C-N) nitrogen atoms. The complexes 1-8 display  $\nu(\text{M}=\text{O})$  modes [30,31] at 840-940  $\text{cm}^{-1}$ . The far IR spectra of 2 and 6 display bands at 445 and 470  $\text{cm}^{-1}$  respectively, which are tentatively attributed to the  $\nu(\text{M}-\text{O})$  modes [32,33] (O=oxygen in organic ligands). The presence of  $\nu(\text{M}-\text{Cl})$  modes [34] in complexes 1-7 at 270-310  $\text{cm}^{-1}$  indicate the coordination of chlorine atom. The IR spectra of the complexes 8 and 9 show characteristic bands of ionic nitrate ( $\sim 1380 \text{ cm}^{-1}$ – $810 \text{ cm}^{-1}$  and  $\sim 720 \text{ cm}^{-1}$ ) [35,36]. This supports the contention that nitrate anions remain outside the coordination sphere as is indicated by the molar conductance values.

**Magnetic moment and electronic spectra.** The magnetic susceptibility measurements on 1-8 and 10 indicate that complexes are diamagnetic (Table 3). These complexes exhibit only charge transfer bands in their electronic spectra (Table 3). These data are consistent with six-fold coordination of the Zr(IV) and U(VI) complexes with octahedral geometry and four-coordinated square planar geometry of zinc (II) complexes.

Copper (II) complex, (9) was found to be paramagnetic giving magnetic moment of 2.07 B.M. corresponding to one unpaired electron. The four-coordinated copper complex may possess either tetrahedral or square planar structures. However regular tetrahedral complexes of copper (II) are very uncommon, because of Jahn - Teller effect. It has been found that the electronic spectra of approximately tetrahedral

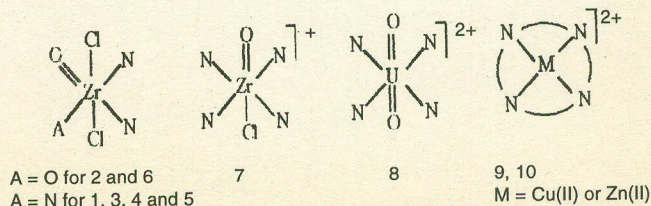
TABLE 3. MAGNETIC MOMENT AND ELECTRONIC SPECTRAL DATA OF THE COMPLEXES.

Compound No.	$\mu_{\text{eff}}$ (B.M.)	$\lambda_{\text{max}}$ (nm)
1	dia	311, 265
2	dia	341, 300, 246
3	dia	341, 310, 277, 248
4	dia	342, 300, 242
5	dia	341, 250
6	dia	344, 251
7	dia	341, 299, 243
8	dia	341, 263
9	2.07	536, 341, 258
10	dia	300, 246

copper (II) complexes display only one band near IR region and no other band in the range 1000 - 500 nm [37]. The electronic spectrum of copper complex in nujol shows bands at 536, 341 and 258 nm. Of these bands, the one at 536 nm may be assigned to a d-d transition of a square planar copper (II).

### Conclusion

From the above discussion, it can be concluded that Zr(IV) and U(VI) complexes, probably, acquire octahedral geometry whereas Zn(II) and Cu(II) complexes assume square planar geometry. Thus the structures of the complexes can be proposed as following.





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