

NEW MIXED COMPLEXES OF Zr (IV) WITH MONO AND MULTIDENTATE LIGANDS

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Several new complexes of zirconium (IV) containing a number of monodentate and multidentate organic ligands have been synthesized and characterized. The complexes have the compositions, $[Zr(O)Cl_2(en).H_2O]$, $[Zr(O)Cl_2.2L.H_2O]$, $[Zr.L'_3Cl]$ and $[Zr(O)Cl_2.L'']$ [*en* = ethylenediamine; *L* = triphenylphosphine oxide, triphenylarsine oxide, pyridine or aniline; *L'* = 8-hydroxyquinoline, *o*-aminophenoxide, *L''* = diethylenetriamine and triethylenetetramine]. The molar conductance data indicate that complexes $[Zr(C_9H_6NO)_3Cl]$ and $[Zr(C_6H_4NH_2O)_3Cl]$ are 1:1 electrolytes but all other complexes behave as 2:1 electrolytes. The experimental data are consistent with six-fold coordination of Zr (IV) ion in all the complexes excepting $[Zr(C_9H_6NO)_3Cl]$, $[Zr(C_6H_4NH_2O)_3Cl]$ and $[Zr(O)Cl_2.tet]$ which are seven coordinated.

Key words: Heteroligand, Zirconium, Complexes.

Introduction

Mixed ligand complexes of transition metal ions are of recent interest and importance in the analytical, biological and industrial fields. Preparation and characterization of mixed ligand complexes of lighter transition metal ions have been reported [1-5]. However, mixed ligand complexes of heavier metal ions have not been well studied. We undertook a program to synthesize a series of such complexes of Zr (IV). We report herein the syntheses of these complexes and investigate into their bondings and structures.

Experimental

Reagents. The chemicals used were of reagent grade as supplied by Merck except for ethanol which was purified by refluxing the 99% crude with magnesium turnings and iodine, and finally distilled and stored over molecular sieves.

Physical measurements and elemental analyses. Infrared spectra of the complexes in KBr were recorded by a Pye-Unicam SP3-300 infrared spectrophotometer. All the spectra were taken in the range $200-4000\text{ cm}^{-1}$ and calibrated against 1601.8 cm^{-1} Peak of polystyrene film. Conductivities of 10^{-3} M solutions of the complexes in dimethylsulfoxide (DMSO) were measured at room temperature using a PTI-18 digitized conductivity meter and a dip-cell with platinized electrodes. The cell was calibrated with 0.01N, 0.001N and 0.0001N KCl solutions.

Micro analyses for C, H and N were performed by the Microanalytical Services of the Department of Chemistry, University of St. Andrews, Scotland.

PREPARATION OF THE COMPLEXES

Preparation of 1, $[Zr(O)Cl_2(en)H_2O]$. Ethylenediamine (0.002 mol) was added to a solution of $Zr(O)Cl_2.8H_2O$ (0.002

mol) in methanol (20 cm^3). The resulting mixture was warmed and stirred. The precipitate thus obtained was separated, washed with ethanol and dried *in vacuo* over P_4O_{10} .

General method of preparation of 2, 3 and 5, $[Zr(O)Cl_2.2L.H_2O]$, [*L* = $OPPh_3$, $OAsPh_3$ or $C_6H_5NH_2$]. To a solution of $ZrOCl_2.8H_2O$ (0.002 mol) in methanol (20 cm^3) was added a solution of ligand *L* (0.004 mol) in ethanol (20 cm^3). The resulting mixture was boiled down to ca. 10 cm^3 and cooled to room temperature. The product was separated, washed with ethanol and dried *in vacuo* over P_4O_{10} .

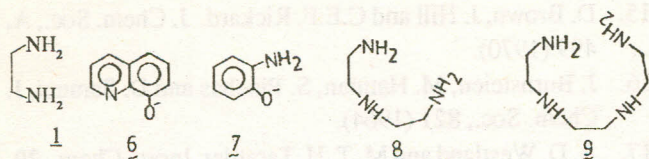
Preparation of 4, $[Zr(O)Cl_2.2C_5H_5N.H_2O]$. A solution of pyridine (0.004 mol in ethanol) (20 cm^3) was added to solution of $ZrOCl_2.8H_2O$ (0.002 mol) in methanol (20 cm^3). The precipitate was separated, washed and stored as above.

Preparation of 6, $[Zr(C_9H_6NO)_3Cl]$. A solution of 8-hydroxyquinoline (0.006 mol) in ethanol (25 cm^3) was added to a solution of $ZrOCl_2.8H_2O$ (0.002 mol) in methanol (20 cm^3). The precipitate formed was filtered, washed with ethanol and stored as above.

Preparation of 7, $[Zr(C_6H_4NH_2O)_3Cl]$. To a solution of $ZrOCl_2.8H_2O$ (0.002 mol) in methanol (20 cm^3) was added a solution of *o*-aminophenol (0.006 mol) in ethanol (20 cm^3). The resulting mixture was heated on a steam bath for 10 mins. the precipitate so obtained was stored as above.

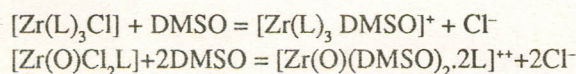
Preparation of 8, $[Zr(O)Cl_2.det]$. Diethylenetriamine (0.002 mol) was added to a solution of $ZrOCl_2.8H_2O$ (0.002 mol) in methanol (20 cm^3). The resulting precipitate was separated, washed with ethanol and stored as above.

Preparation of 9, $[Zr(O)Cl_2.tet]$. The complex was prepared similarly from $ZrOCl_2.8H_2O$ (0.002 mol) in methanol (20 cm^3) and triethylenetetramine (0.002 mol) in ethanol (20 cm^3). The complex was separated and stored as above.



Results and Discussion

The analytical and molar conductance data are shown in Table 1. The complexes 1, 2, 3, 4, 5 and 8 are consistent with six-fold co-ordination and the complexes 6, 7, and 9 are seven-coordinated. The molar conductances measured in DMSO reveal that the complexes 6 and 7 are 1:1 and all other complexes are 2:1 electrolytes [6,7]. This conductance arises because of solvation by DMSO,



where L refers to the unidentate, bidentate, tridentate and tetradentate ligands. The IR spectra of the complexes 1 - 5

in $\nu(\text{P}=\text{O})$ of 22 cm^{-1} compared to the free ligand value (1192 cm^{-1}) [15], suggesting co-ordination by the oxygen of OPPh_3 . Complex 3 shows a decrease in $\nu(\text{As}=\text{O})$ of 20 cm^{-1} from the free ligand value (880 cm^{-1}) [16], indicating co-ordination by the oxygen of OAsPh_3 . It is noteworthy that a shift of $\sim 20\text{ cm}^{-1}$ of $\text{E}=\text{O}$ ($\text{E}=\text{P}$ or As) band indicates that the phosphino or arsino ligand is probably weakly linked with the metal ion. In addition, the far IR spectra of 1 - 7 display bands at $420 - 480\text{ cm}^{-1}$ which are tentatively attributed to the $\nu(\text{M}-\text{O})$ modes [17-21]. ($\text{O}=\text{oxygen}$ of organic ligand). The complexes 1 - 5, 8 and 9 show bands at $950 - 1000\text{ cm}^{-1}$ assignable to $\nu(\text{Zr}=\text{O})$ mode, higher than the reported literature values [19]. This coordinated oxo moiety is presumably very strained because of considerable steric repulsion from other bulky auxiliary ligands in the complexes - thus causing shifting of $\text{Zr}=\text{O}$ bands to higher frequencies. The $\nu(\text{O}-\text{H})$ bands observed in the free 8-hydroxyquinoline and 2-aminophenol disappear in complexes 6 and 7 indicating coordination by the oxygen site.

TABLE 1. ANALYTICAL DATA AND OTHER PHYSICAL PROPERTIES OF THE MIXED LIGAND COMPLEXES OF ZR (IV)*.

No.	Compound	Colour	Calcd. (Found) %			Molar conductance $\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$
			C	H	N	
1.	$[\text{Zr}(\text{O})\text{Cl}_2(\text{en})\cdot\text{H}_2\text{O}]$	White	9.4 (9.1)	3.9 (3.9)	10.9 (10.7)	58
2.	$[\text{Zr}(\text{O})\text{Cl}_2\cdot 2\text{OPPh}_3\cdot\text{H}_2\text{O}]$	White	57.4 (57.4)	4.3 (4.1)	-	60
3.	$[\text{Zr}(\text{O})\text{Cl}_2\cdot 2\text{OAsPh}_3\cdot\text{H}_2\text{O}]$	White	51.4 (51.2)	3.8 (3.8)	-	65
4.	$[\text{Zr}(\text{O})\text{Cl}_2\cdot 2\text{C}_5\text{H}_5\text{N}\cdot\text{H}_2\text{O}]$	White	33.9 (33.7)	3.4 (3.4)	7.9 (7.8)	62
5.	$[\text{Zr}(\text{O})\text{Cl}_2\cdot 2\text{C}_6\text{H}_5\text{NH}_2\cdot\text{H}_2\text{O}]$	Brown	37.7(37.6)	4.2 (4.1)	7.3 (7.2)	59
6.	$[\text{Zr}(\text{C}_9\text{H}_6\text{NO})_3\text{Cl}]$	Yellow	58.0(58.0)	3.2 (3.1)	7.5 (7.5)	28
7.	$[\text{Zr}(\text{C}_6\text{H}_4\text{NH}_2\text{O})_3\text{Cl}]$	Black	47.9(47.7)	4.1 (4.0)	9.3 (9.1)	30
8.	$[\text{Zr}(\text{O})\text{Cl}_2\cdot \text{det}]$	White	17.1 (17.0)	4.7 (4.5)	14.9 (14.8)	61
9.	$\text{Zr}(\text{O})\text{Cl}_2\cdot \text{tet}]$	White	22.2 (22.2)	5.6 (5.4)	17.3 (17.7)	58

* The organic moieties for the compounds indicated are:

exhibit bands at $3400 - 3480\text{ cm}^{-1}$ arising from the coordinated water molecules. Complexes 1, 5, 8 and 9 show two bands, (1, 3180 and 3080 cm^{-1}), (5, 3060 and 2980 cm^{-1}), (8, 3120 and 3090 cm^{-1}) (9, 3060 and 2980 cm^{-1}) and 7 shows a broad band at ($3270 - 3400\text{ cm}^{-1}$) significantly lower than the values for ethylenediamine ($3260, 3180\text{ cm}^{-1}$); aniline ($3440, 3360\text{ cm}^{-1}$); 2-aminophenol ($3414, 3342\text{ cm}^{-1}$); diethylenetriamine ($3360, 3290\text{ cm}^{-1}$) and triethylenetetramine ($3380, 3300\text{ cm}^{-1}$) which indicate co-ordination by the amino nitrogen. This is also evident from the appearance of $\nu(\text{M}-\text{N})$ at $325 - 390\text{ cm}^{-1}$ in the far IR spectra of the complexes (1, 4-9) [8-10]. In complexes 4 and 6 the $\nu(\text{C}=\text{N})$ modes appear at 1540 and 1555 cm^{-1} respectively, relative to the free ligand value (1610 cm^{-1}) indicating that the ring nitrogen is co-ordinated to the metal atom [11-13]. All complex exhibit bands at $266 - 310\text{ cm}^{-1}$, tentatively assigned to the $\nu(\text{Zr}-\text{Cl})$ mode [14]. Complex 2 shows a decrease

References

1. M. T. H. Tarafder and M. Rahim, *Ind. J. Chem.*, **28A**, 1105 (1989).
2. M. T. H. Tarafder and K. Fatema, *Ind. J. Chem.*, **27A**, 444 (1988).
3. M. T. H. Tarafder, K. Fatema and M. A. J. Miah, *J. Bangladesh Chem. Soc.*, **2**, 47 (1989).
4. M. A. Ali, P. Ghosh, M. Nazimuddin, S. M. H. Majumder, T. H. Tarafder and A. Khair, *J. Bangladesh Chem. Soc.*, **3**(1), 25 (1990).
5. M. T. H. Tarafder and K. Fatema, *J. Bangladesh Chem. Soc.*, **1**, 77 (1988).
6. M. T. H. Tarafder, A. R. Khan and B. Nath, *J. Bangladesh Chem. Soc.*, **1**(2), 149 (1988).
7. W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
8. M. T. H. Tarafder and M. A. Ali, *Can. J. Chem.*,

- 56, 2000 (1978).
9. M. T. H. Tarafder, M. A. J. Miah, R. N. Bose and M. A. Ali, *Inorg. Nucl. Chem.*, **43**, 3151 (1981).
 10. M. A. Ali and R. N. Bose, *Polyhedron*, **3**, 520 (1984).
 11. M. T. H. Tarafder and M. A. L. Miah, *Inorg. Chem.*, **25**, 2265 (1986).
 12. S. E. Jacobsor, R. Tang and F. Mares, *Inorg. Chem.*, **17**, 3055 (1978).
 13. H. Minoun, M. Oosted, F. Casabianca, J. Fischer and A. Mitschler, *Inorg. Chem.*, **21**, 1303 (1982).
 14. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Co-ordination Compounds* (John Wiley & Sons, New York, 1978), 3rd edn., pp 317.
 15. D. Brown, J. Hill and C.E.F. Rickard, *J. Chem. Soc., A*, 499 (1970).
 16. J. Burnsteien, M. Hatman, S. Pinchas and D. Samuel, *J. Chem. Soc.*, 821 (1964).
 17. A. D. Westland and M. T. H. Tarafder, *Inorg. Chem.*, **20**, 3992 (1981).
 18. A. D. Westland and M. T. H. Tarafder, *Inorg. Chem.*, **21**, 3228 (1982).
 19. M. T. H. Tarafder, P. Bhattacharjee and A. K. Sarkar, *Polyhedron*, **11**, 795 (1992).
 20. M. T. H. Tarafder and A. Ahmed, *Ind. J. Chem.*, **25A**, 729 (1986).
 21. M. T. H. Tarafder, *Ind. J. Chem.*, **26A**, 874 (1987).