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## Thorium(IV) and Zirconium(IV) Complexes of Oxygen Donor Ligands, Part XI. Oxozirconium(IV) Complexes of Hexamethyl Phosphoramidate\*

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A series of new complexes of the type  $ZrOX_2(HMPA)_n$  ( $n = 2$  for  $X = NO_3, Cl, Br, I, BPh_4, NCS$ ;  $n = 6$  for  $X = ClO_4$ ) are described. The coordination number of the zirconium was found to be 5 or 7 depending on the nature of anion X.

We have earlier reported<sup>1-6</sup> the oxozirconium(IV) complexes of several oxygen donor ligands containing the  $X=O$  group (where  $X = C, N, S$  or  $P$ ). We have shown<sup>2</sup> that triphenylphosphine oxide (TPPO) coordinates with oxozirconium(IV) through the lone oxygen atom. A related phosphoryl donor, hexamethylphosphoramidate(HMPA), having a high dipole-moment<sup>7</sup> and solvent properties<sup>8</sup>, has been used as a complexing agent for various transition and non-transition metals<sup>9</sup>. In the present work, some new oxozirconium(IV) complexes of HMPA are described.

### RESULTS AND DISCUSSION

The analytical and other physical data on all the complexes are reported in Table I. The complexes are quite stable at room temperature except for the iodo complex, which slowly decomposes to a sticky mass. The complexes are sufficiently soluble in polar solvents and insoluble in non-polar solvents. The molar conductance values in  $PhNO_2$  and DMSO show that chloro, bromo, nitrate, thiocyanato and tetraphenylboronato complexes are non-electrolytes, while iodo and perchlorato complexes behave like uni-bivalent electrolytes. The molecular weights, determined cryoscopically in freezing  $PhNO_2$ , support the same electrolytic behaviour of the complexes. The magnetic measurements of the complexes show them to be diamagnetic.

Hexamethylphosphoramidate  $(CH_3)_2N_3PO$ , has four possible coordination sites, the oxygen atom and the three nitrogen atoms. It is well known that the

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TABLE I  
Analytical, Conductivity, Molecular Weight Data for the HMPA Complexes of Oxoirconium(IV)

Compound	Colour	Found (Calcd.)%			Anion	$\Lambda_m$ ohm <sup>-1</sup> cm <sup>2</sup> mole <sup>-1</sup>	Electrolytic nature	Mol. Wt. Found (Calcd)
		Zr	P	O				
ZrO(ClO <sub>4</sub> ) <sub>2</sub> · 6HMPA	White	6.35 (6.6)	13.3 (13.5)	14.1 (14.4)	48.3 <sup>b</sup> , 79.7 <sup>c</sup>	1 : 2	435 (1380)	
ZrO(NO <sub>3</sub> ) <sub>2</sub> · 2HMPA	White	15.1 (15.4)	10.7 (10.5)	—	—	Non-electrolyte	— (589)	
ZrOCl <sub>2</sub> · 2HMPA	White	16.8 (17.0)	11.35 (11.6)	13.6 (13.2)	4.9 <sup>b</sup> , 11.7 <sup>c</sup>	Non-electrolyte	492 (536)	
ZrOBr <sub>2</sub> · 2HMPA	White	14.9 (14.6)	9.65 (9.9)	24.9 (25.6)	4.6 <sup>b</sup> , 9.3 <sup>c</sup>	Non-electrolyte	590 (625)	
ZrOI <sub>2</sub> · 4HMPA	Yellow	8.1 (8.4)	11.3 (11.5)	22.95 (23.6)	50.7 <sup>b</sup> , 81.3 <sup>c</sup>	1 : 2	338 (1077)	
ZrO(BPh <sub>4</sub> ) <sub>2</sub> · 2HMPA	White White	8.0 (8.25)	5.35 (5.6)	—	—	Non-electrolyte	— (1103)	
ZrO(NCS) <sub>2</sub> · 2HMPA	pink	15.9 (15.7)	10.95 (10.7)	19.35 (20.00)	9.6 <sup>b</sup> , 18.7 <sup>c</sup>	Non-electrolyte	552 (581)	

<sup>a</sup> — insoluble, <sup>b</sup> — in PhNO<sub>2</sub>, <sup>c</sup> — DMSO

nitrogen atom is more basic than the oxygen atom. In HMPA the nitrogen lone pair electrons involved in  $\pi$ -bonding with empty d-orbitals of the phosphorus atom reduces the basicity of the nitrogen atoms; hence the HMPA ligand coordinates with metal ions through its lone oxygen atom<sup>9</sup>.

The infrared spectra of the ligand and its complexes show that the  $\nu$  (P=O) observed at ca. 1220  $\text{cm}^{-1}$  in free ligand<sup>9,10</sup> suffers a significant negative shift on complexation due to decrease in  $p_{\pi}\text{O}-d_{\pi}\text{P}$  back bonding (Table II). Thus, it is concluded the HMPA ligand coordinates only through its oxygen atom. The P—N stretching frequencies assigned at ca. 980 and 745  $\text{cm}^{-1}$  in the free ligand<sup>9</sup> are either unaffected or suffer slight positive shift on complexation. This also precludes the possibility of coordination through the nitrogen atom of the Lewis base. The P=O bending of HMPA at 480  $\text{cm}^{-1}$  is observed to undergo a positive shift in its adducts. The metal-ligand vibration in these complexes has been assigned in 400—350  $\text{cm}^{-1}$  region<sup>1,2,11,12</sup>.

TABLE II  
Partial IR Spectral Data<sup>a</sup> of HMPA and its Complexes

Compound	$\nu$ (P = O)	$\nu$ (P—N)	$\delta$ (P—O)	$\nu$ (M—O)
HMPA	1220vs	980m 745m	480m	400m
ZrO(ClO <sub>4</sub> ) <sub>2</sub> · 6HMPA	1140s	980m 750m	480m	300m
ZrO(NO <sub>3</sub> ) <sub>2</sub> · 2HMPA	1150s	985m 745m	490m, br	405m, br
ZrOCl <sub>2</sub> · 2HMPA	1155s	980m 750m	458m, br	390m
ZrOBr <sub>2</sub> · 2HMPA	1145s	985m 750m	480m	380m
ZrOI <sub>2</sub> · 4HMPA	1170s	980m 750m	485m	380w
ZrO(BPh <sub>4</sub> ) <sub>2</sub> · 2HMPA	1160s	990m 750m	485m	380m
ZrO (NCS) <sub>2</sub> · 2HMPA	1180s	990m 750m	485m, br	385m

<sup>a</sup> In  $\text{cm}^{-1}$

The Zr=O characteristic band is observed in all the complexes as a weak band in the 980—900  $\text{cm}^{-1}$  region<sup>2,11,13</sup>.

In the perchlorato complex the very strong  $\nu_3$  band and a strong  $\nu_4$  band appear at ca. 1080 and 620  $\text{cm}^{-1}$ , respectively for perchlorate ions, indicating that the  $T_d$  symmetry has not been disturbed and the perchlorate ions are not bonded to the zirconium ion<sup>1,2,11,12</sup>. The absence of the  $\nu_3$  band of ionic nitrate  $D_{3h}$  around 1360  $\text{cm}^{-1}$  and the occurrence of two strong bands at ca. 1525 ( $\nu_4$ ) and 1300  $\text{cm}^{-1}$  ( $\nu_1$ ) in the spectrum of ZrO(NO<sub>3</sub>)<sub>2</sub> · 2HMPA suggest the coordination of nitrate ions in this complex<sup>14,15</sup>. The two combination bands ( $\nu_1 + \nu_4$ ) appeared as weak bands at ca. 1760 and 1720  $\text{cm}^{-1}$  in the spectra. By applying the 'Lever separation method'<sup>16</sup>, the separation of 40  $\text{cm}^{-1}$  in this case, suggests the bidentate

nature of the nitrate groups. The presence of bands at ca. 1030 ( $\nu_2$ ), 800 ( $\nu_6$ ) and 735  $\text{cm}^{-1}$  ( $\nu_3/\nu_5$ ) further confirm the bidentate nature of the nitrate groups<sup>17</sup>. The IR spectrum of the thiocyanato complex shows bands at ca. 2050  $\nu$  (CN), 780  $\nu$  (CS) and 470  $\text{cm}^{-1}$   $\delta$  (NCS), which are attributable to the N-bonded thiocyanate groups<sup>18,19</sup>.

On comparing the IR spectra of  $\text{ZrO}(\text{BPh}_4)_2 \cdot 2\text{HMPA}$  with that of sodium tetraphenylboron<sup>20,21</sup> in the 1500—1350  $\text{cm}^{-1}$  region, it is found that the IR spectrum of tetraphenylboronato complex has four strong bands at 1480, 1455, 1430 and 1390  $\text{cm}^{-1}$  which conclusively indicate the coordination of tetraphenylboronate to the zirconium(IV) ion through a  $\pi$ -bond of a phenyl ring<sup>3,20,21</sup>.

Thus the coordination number of zirconium(IV) in these complexes is five or seven depending upon the presence of anions.

#### EXPERIMENTAL

Lewis acids were obtained as reported previously<sup>3,4</sup>, while HMPA was obtained from BDH. The complexes were prepared by the following general method. A solution of metal salt in MeOH was treated with a slight excess of HMPA in the same solvent. The thiocyanato complex was precipitated immediately, while others were obtained by refluxing the reaction mixture for ca. 3h and removing the excess solvent by distillation. The residual mass on treatment with  $\text{Et}_2\text{O}$  yielded a crystalline solid which was filtered and washed with  $\text{Et}_2\text{O}$  and dried in vacuo over  $\text{P}_4\text{O}_{10}$ .

$\text{ZrO}(\text{BPh}_4)_2 \cdot 2\text{HMPA}$  was prepared by mixing the  $\text{Me}_2\text{CO}$  solutions of metal salt and HMPA and leaving the reaction mixture overnight. Crystalline complex separated out and washed with  $\text{Me}_2\text{CO}$  and finally with  $\text{Et}_2\text{O}$  and dried as above.

The metal and anion analyses and physical measurements of the complexes were made as reported previously<sup>4</sup>, while the phosphorus was estimated by the standard method<sup>22</sup>.

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### SAŽETAK

#### **Kompleksi torija(IV) i cirkonija(IV) s ligandima koji sadržavaju kisik kao donor. XI. Oksocirkonijevi(IV) kompleksi s heksametilfosforamidom**

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Opisana je priprava niza kompleksa cirkonija(IV) s heksametil-fosforamidom (HMPA). Na osnovi analitičkih podataka te konduktometrijskih i krioskopskih određivanja sastav proučavanih kompleksa može se općenito prikazati kao  $ZrOX_2(HMPA)_n$  ( $n = 2$  za  $X = NO_3, Cl, Br, I, BPh_4, NCS$ ;  $n = 6$  za  $X = ClO_4$ ). Iz intracrvenih spektara proizlazi da koordinacijski broj cirkonija u proučavanim kompleksima iznosi 5 ili 7, ovisno o vrsti aniona X.

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