

Result and Discussion

Schiff bases react very easily with Zinc(II) acetate, yielding 1:2 complexes of the type  $ZnL_2$ , having brilliant yellow colour indicating deprotonation of ligands from the reactive phenolic  $-OH$  group. In case of disalicylaldimine sulphaguanidine ( $H_2SG$ ), however, 1:1 complex was obtained. Loss of weight shows that one water molecule was associated with Zinc(II) complex of disalicylaldimine sulphaguanidine. The complexes are insoluble in water and common organic solvents like chloroform, carbon tetrachloride, benzene, etc. but soluble in formamide and dimethylformamide. Most of the complexes undergo charring between  $200-300^\circ C$  without melting, indicating that they are co-ordination polymers which usually decompose without melting. The molecular weight determinations in formamide solutions (as the complexes are insoluble in non-polar solvents) correspond to monomer species which may be due to breakdown of ligand bridges by formamide molecules.

The electronic spectra  $Zn^{II}(d^{10})$  Schiff base complexes in nujol are almost identical with those of other similar Schiff base complexes<sup>8</sup>. In non-donor solvents the corresponding absorption maxima lie at nearly identical frequencies which suggest that the complexes are either tetrahedral or pseudo-octahedral due to weak interaction with sulfone ( $-SO_2-$ ) group.

The i.r. spectra of HL or  $H_2L$  and their Zinc(II) complexes in general show absence of  $\nu OH$  and presence of  $\nu NH$  of the ligand in the complexes. A close examination of the spectra reveals that the  $\nu NH$  band in most of the Zinc(II) complexes shift to higher frequencies. In  $H_2L$  complex, however, there are two additional bands at  $3480\text{ cm}^{-1}$  and  $3430\text{ cm}^{-1}$  which may be due to  $\nu OH$  of the associated water molecule. The  $\nu C=N$  appears lower shifted from  $1640-1610\text{ cm}^{-1}$  to  $1620-1600\text{ cm}^{-1}$  in complexes. Besides  $\nu NH$ ,  $\nu OH$  and  $\nu C=N$  bands, HL have sulfone ( $-SO_2-$ ) group, which is characterised by strong broad bands<sup>9</sup>  $\nu'$  between  $1380-1300\text{ cm}^{-1}$  and  $\nu''$  between  $1180-1100\text{ cm}^{-1}$ . These bands are either unaffected or observed slightly affected, signifying either the absence or the weak co-ordination through  $-SO_2-$  group. The authors favour the latter conclusion as the same is also supported by electronic spectra as discussed above.

A number of other bands due to phenyl  $-CH$  and R substituents<sup>10</sup> at N', viz., guanidine, dimidine, thiazole, merazine, diazine and acetyl group are either unaffected or slightly affected on chelation through salicylaldimine part.

Authors thank Dr. S. Ghosal, Head, Department of Pharmaceutics, I.T., B.H.U. for laboratory facilities and to Prof. B. M. Shukla, Head, Department of Chemistry, B.H.U., for allowing to record infrared

electronic spectra and for nitrogen microanalysis. One of us (U. S. K.) thanks Banaras Hindu University for the financial assistance.

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STUDIES ON Th(IV) AND Zr(IV) COMPLEXES  
OF OXYGEN DONOR LIGANDS—X

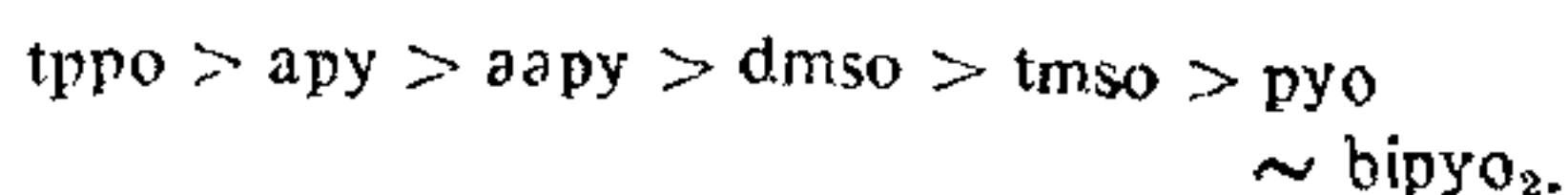
$\pi$ -Bonded Complexes of Oxygen Donor Ligands with  
Oxozirconium(IV) Tetrphenylboronate\*

As part of our studies on oxygen ligands<sup>1-4</sup>, efforts were made for the first time to stabilise oxozirconium (IV) in the presence of tetrphenylboronate anion  $[BPh_4]^-$  in non-aqueous media by using strongly basic oxygen donor ligands such as antipyrine (apy), 4-amino antipyrine (aapy), pyridine N-oxide (pyo), 2,2'-bipyridyl-N-N'-dioxide (bipyo<sub>2</sub>), dimethyl sulphoxide (dmsO), tetramethylene sulphoxide (tmsO) and triphenylphosphine oxide (tppo). The ligands of interest, having an oxygen atom bonded to a non-metal atom, are quite polar molecules as indicated by their dipole-moments : 5.48D for apy<sup>5</sup>; 4.24D for pyo<sup>6</sup> and 3.9 and 4.28D for dmsO<sup>7</sup> and tppo<sup>8</sup>

respectively and therefore are good oxygen donors<sup>1-4,7</sup> towards metal ions.

Stoichiometries of the isolated complexes have been established by elemental analyses (Table I). All the complexes, except of dmsO, are non-hygroscopic and are quite stable. The complexes are sufficiently soluble in common organic solvents. The apy, aapy, dmsO and tmsO complexes of ZrO(BPh<sub>4</sub>)<sub>2</sub> are non-electrolytes, whereas bipyo<sub>2</sub> and tppo complexes appear to be univalent in nature (Table I). The molecular weight determinations (Table I) in nitrobenzene also support the above mentioned electrolytic behaviour.

the metal and ligands. The i.r. spectral studies reveal the relative order of the donor strength of ligands as,



In apy and aapy complexes the  $\nu(\text{CN})$  frequency have been assigned at ca. 1320 and 1340  $\text{cm}^{-1}$ , respectively; which goes a positive shift on complexation<sup>9</sup>. In aromatic amine N-oxides, i.e., pyO and bipyo<sub>2</sub> the absolute assignment for  $\nu(\text{CN})$  stretching is, not possible. C=C, C=N stretchings and ring vibrations at ca. 1610 and 1475  $\text{cm}^{-1}$  in case of pyO<sup>10</sup> and

TABLE I  
Analytical data of oxozirconium(IV) complexes

Complex	M. pt. °C	Found (Calcd.) %				Molar conductance m ohm <sup>-1</sup> cm <sup>2</sup> mole <sup>-1</sup>	Electrolytic nature	Mol. wt. found (Calcd.)
		Zr	C	H	X <sup>a</sup>			
ZrO(BPh <sub>4</sub> ) <sub>2</sub> · 2apy	170	7.98 (8.11)	48.76 (49.24)	3.82 (3.92)	5.14 (4.99)	4.3	Non-electrolyte	1089 (1121)
ZrO(BPh <sub>4</sub> ) <sub>2</sub> · aapy	183	9.23 (9.59)	43.71 (44.30)	3.82 (3.48)	3.98 (4.43)	3.7	Non-electrolyte	897 (948)
ZrO(BPh <sub>4</sub> ) <sub>2</sub> · 4pyO	210d	8.02 (8.08)	45.38 (46.93)	3.51 (3.55)	4.76 (4.97)	xx	..	..
ZrO(BPh <sub>4</sub> ) <sub>2</sub> · 2bipyo <sub>2</sub>	230d	8.02 (8.11)	47.97 (47.10)	3.08 (3.21)	4.80 (4.99)	55.5	1 : 2	410 (1121)
ZrO(BPh <sub>4</sub> ) <sub>2</sub> · 2dmsO	110	9.98 (10.09)	36.73 (37.29)	3.42 (3.55)	7.28 (7.10)	5.6	Non-electrolyte	859 (901)
ZrO(BPh <sub>4</sub> ) <sub>2</sub> · 2tmsO	153	9.63 (9.54)	40.92 (40.29)	3.63 (3.77)	6.60 (6.71)	4.9	Non-electrolyte	920 (953)
ZrO(BPh <sub>4</sub> ) <sub>2</sub> · 4tppo	160	4.81 (4.90)	61.76 (62.03)	4.09 (4.30)	6.52 (6.67)	59.9	1 : 2	680 (1857)

d = decomposed; X<sup>a</sup> = N, S or P; xx = insoluble.

The infra-red spectra of the free ligands and the complexes were recorded in the 4000–400  $\text{cm}^{-1}$  region. The i.r. studies reveal bidentate nature of aapy and bipyo<sub>2</sub> coordination occurring through amino nitrogen and carbonyl oxygen in case of aapy and through both the oxygen atoms of bipyo<sub>2</sub>; rest of the ligands link only through the lone oxygen atom. The position of the X = O (X = C, N, P or S) stretching vibrations in the complexes differs greatly from those in the free ligands (Table II) and are comparable to those published for similar complexes<sup>1-4,7</sup>. A marked negative shift in  $\nu(\text{X}=\text{O})$  from free ligands in all the complexes confirm the oxygen linkage between

1430 and 1400  $\text{cm}^{-1}$  in case of bipyo<sub>2</sub><sup>11</sup> have been assigned. As expected no significant change has been observed in these modes after complexation.

On comparing the i.r. spectra of sodium tetraphenylboron<sup>12,13</sup> and the complexes in the 1500–1350  $\text{cm}^{-1}$  region, it is found that in case of apy, aapy, dmsO and tmsO complexes the i.r. spectra have four distinct strong bands in this region (Table II), which conclusively indicates the coordination of tetraphenylboronate to zirconium(IV) ion through a  $\pi$ -bond of a phenyl ring<sup>12-14</sup>. The other pyO, bipyo<sub>2</sub> and tppo complexes have only two strong bands at ca. 1480 and 1435  $\text{cm}^{-1}$  showing



TABLE II  
Infrared data ( $\text{cm}^{-1}$ ) of oxozirconium complexes

Complex	$\nu(\text{X}=\text{O})$ (X = C, N, S, or P)		$\Delta$ $\nu(\text{X}=\text{O})$	C=N stretchings	$\nu(\text{Zr}=\text{O})$	Anion vibrations
	Ligand	Complex				
ZrO(BPh <sub>4</sub> ) <sub>2</sub> · 2apy	1660s	1580s	80	1340s	970w	1480s, 455m, 1430m, 1390s
ZrO(BPh <sub>4</sub> ) <sub>2</sub> · aapy	1670s 1640s	1590s	65	1355s	972w	1485s, 1460m, 1430s, 1360m
ZrO(BPh <sub>4</sub> ) <sub>2</sub> · 4pyo	1265s	1222s	43	1608w 1470s	965m	1480s, 1430s
ZrO(BPh <sub>4</sub> ) <sub>2</sub> · 2bipyO <sub>2</sub>	1265s	1220s	45	1448s 1420m	960w	1480s, 1435s
ZrO(BPh <sub>4</sub> ) <sub>2</sub> · 2dmso	1055s	1000s	55	..	970w	1480s, 1460s, 1435m, 1380m
ZrO(BPh <sub>4</sub> ) <sub>2</sub> · 2tmso	1020s	970s	50	..	..	1480s, 1460s, 1430s, 1390s
ZrO(BPh <sub>4</sub> ) <sub>2</sub> · 4tppo	1195s	1110s	85	..	980w	1485s, 1440s
[Na] <sup>+</sup> [BPh <sub>4</sub> ] <sup>-</sup>	..	..	..	..	..	1480s, 1452vw, 1425s, 1390vw <sup>b</sup>

*b* = assigned to in plane skeletal C-C stretching modes of phenyl ring (Ref. 12).

the presence of uncomplexed tetraphenylboronate ion in these complexes<sup>12</sup>.

A medium intensity band in 980-960  $\text{cm}^{-1}$  region is assigned as (Zr = O) stretching mode in all the complexes<sup>11,16</sup>.

Thus, the coordination number of zirconium(IV) in these complexes is five.

#### Experimental

Oxozirconium(IV) tetraphenylboronate was prepared in solution by mixing acetone solutions of anhydrous ZrOCl<sub>2</sub><sup>16</sup> and NaBPh<sub>4</sub> and filtering out the precipitated NaCl.

Oxozirconium(IV) tetraphenylboronate (1m mole) solution, obtained as above, was mixed with acetone (20 ml) solutions of respective ligands (4m mole) and left the reaction mixture overnight. Crystalline complex separated out in all cases except the dmso complex which was precipitated by adding an excess of anhydrous diethyl ether. The complexes were washed thoroughly with acetone and dried *in vacua* over P<sub>4</sub>O<sub>10</sub>. Yield 60-70%.

Thanks are due to U.G.C., New Delhi, for financial support.

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\* Presented at Annual Convention of Chemists, 1979, September 23-27, Kurukshetra University, Kurukshetra.

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