

Note

INFRARED AND THERMAL INVESTIGATIONS OF OXOZIRCONIUM(IV) HALIDE COMPLEXES WITH SOME HETEROCYCLIC BASES

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In previous communications [1,2], oxozirconium(IV) perchlorate, nitrate and thiocyanate complexes of heterocyclic bases were reported. Halogens are common ligands in coordination chemistry, readily forming coordinate bonds with metals. Comparatively less is known about the oxozirconium(IV) halide complexes of heterocyclic bases (3). Therefore, it was thought worthwhile to extend the investigation to the oxozirconium(IV) halides. In this communication, we report some oxozirconium(IV) complexes of the general composition, $ZrOX_2 \cdot nL$. Where $n = 4$, $L =$ pyridine (py), α -picoline (pic), 2-aminopyridine (NH_2 py), 2,4-lutidine (2,4LN), 2,6-lutidine (2,6LN) and quinoline (Q), and where $n = 2$, $L =$ 2,2'-bipyridyl (bipy) and 1,10-phenanthroline (phen), while $X = Cl^-$, Br^- or I^- .

EXPERIMENTAL

All Lewis bases and solvents employed were obtained commercially and purified wherever necessary. Oxozirconium(IV) chloride was obtained from Reidal, while the bromide and iodide were prepared from the chloride as reported earlier [4].

Complexes were prepared in methanol by reacting metal salts with the ligands in the required molar ratio. Some complexes separated out either immediately or after some time, whereas some required refluxing for 1 h and standing overnight. All the complexes were filtered, washed with methanol followed by ether and dried in vacuo over P_4O_{10} . The analysis and physical measurements were performed as reported previously [4].

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TABLE I
Analytical data on the complexes of Zr(IV)

Complex	Analysis (%)					
	Metal		Halogen		Nitrogen	
	Found	Calcd.	Found	Calcd.	Found	Calcd.
ZrOCl ₂ ·4 (py)	18.30	18.46	14.30	14.34	11.38	11.33
ZrOCl ₂ ·4 (pic)	16.40	16.58	12.80	12.88	10.00	10.17
ZrOCl ₂ ·4 (NH ₂ py)	16.36	16.46	12.88	12.79	20.10	20.21
ZrOCl ₂ ·4 (2,4 LN)	15.10	15.04	11.78	11.69	9.28	9.24
ZrOCl ₂ ·4 (2,6 LN)	15.12	15.04	11.76	11.69	9.32	9.24
ZrOCl ₂ ·4 (Q)	13.20	13.14	10.10	10.21	8.16	8.06
ZrOCl ₂ ·2 (bipy)	18.45	18.61	14.40	14.46	11.32	11.42
ZrOCl ₂ ·2 (phen)	17.06	16.95	13.00	13.17	10.30	10.40
ZrOBr ₂ ·4 (py)	15.78	15.64	27.32	27.41	9.45	9.60
ZrOBr ₂ ·4 (pic)	14.34	14.27	25.10	25.00	8.76	8.76
ZrOBr ₂ ·4 (NH ₂ py)	14.28	14.18	24.92	24.85	17.34	17.41
ZrOBr ₂ ·4 (2,4 LN)	13.00	13.12	22.10	22.99	8.00	8.05
ZrOBr ₂ ·4 (2,6 LN)	13.22	13.12	22.12	22.99	7.92	8.05
ZrOBr ₂ ·4 (Q)	11.78	11.65	20.40	20.41	6.98	7.15
ZrOBr ₂ ·2 (bipy)	15.60	15.75	27.45	27.60	9.52	9.67
ZrOBr ₂ ·2 (phen)	14.48	14.54	25.42	25.48	8.82	8.93
ZrOI ₂ ·4 (py)	13.40	13.47	37.40	37.48	8.30	8.27
ZrOI ₂ ·4 (pic)	12.34	12.44	34.60	34.62	7.60	7.63
ZrOI ₂ ·4 (NH ₂ py)	13.30	12.37	34.40	34.43	15.10	15.19
ZrOI ₂ ·4 (2,4 LN)	11.50	11.56	32.10	32.16	7.00	7.09
ZrOI ₂ ·4 (2,6 LN)	11.52	11.56	28.90	28.93	7.18	7.09
ZrOI ₂ ·4 (Q)	10.32	10.40	37.62	37.71	6.32	6.38
ZrOI ₂ ·2 (bipy)	13.42	13.55	37.54	37.74	8.25	8.32
ZrOI ₂ ·2 (phen)	12.52	12.65	35.00	35.20	7.60	7.76

RESULTS AND DISCUSSION

The analytical data on the newly synthesised complexes are summarised in Table 1. The chloro and bromo complexes are white, while iodo complexes are yellow crystalline solids. The molar conductance in nitrobenzene indicates the non-electrolytic nature of the complexes. The chloro and bromo complexes are non-hygroscopic, while iodo complexes absorb moisture from the atmosphere after keeping for some time. The molecular weight determination of some of the complexes, which was carried out cryoscopically in freezing nitrobenzene, also supports the similar electrolytic behaviour of the complexes.

Infrared

Singh [5] and Ferraro et al. [6–8] have widely investigated the infrared spectra of the ligands and their metal complexes. The most intense and characteristic bands in the vibrational spectra of heterocyclic bases and their adducts, appear in the 1600–1400 cm^{-1} region. All of these bands involve C–C, C–N and ring stretching. The absorptions associated with the cyclic ring are apparently unaffected on complexation (not listed), while those arising from the heterocyclic ring are shifted to higher frequencies, due to contraction of the ring on coordination. Because of poor resolution, any discussion of the region beyond 1600 cm^{-1} is not useful. The largest shift in frequency is found with vibrations involving C–C and C–N stretching modes. This is expected, as the coordination takes place through the hetero *N* atom and the effect is transmitted throughout the region, resulting in the readjustment of electron density [1,5,7]. In NH_2py the strong band at 3333 cm^{-1} , attributed to the $-\text{NH}_2$ group, is not affected, while the other frequencies affected on complexation clearly indicate that in NH_2py the coordination takes place with the hetero *N* atom [5,9,10]. If the magnitude of the frequency shift * on coordination is any indication of acceptor strength, the order $\text{ZrOCl}_2 > \text{ZrOBr}_2 > \text{ZrOI}_2$ will emerge.

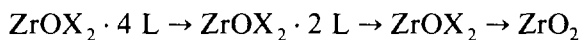
From simple electronegativity considerations or from calculations of *d* orbital contraction, the chlorides are expected to be the best acceptors of all the halides and the order $\text{F} > \text{Cl} > \text{Br} > \text{I}$ is obtained with respect to the effect of the central atom [11,12].

The metal–ligand vibration in these complexes has been tentatively assigned in the 390–320 cm^{-1} region [1,2]. The $\nu(\text{Zr}-\text{Cl})$ vibration has been assigned at about 300 cm^{-1} in these complexes [13,14], while $\nu(\text{Zr}-\text{Br})$ and $\nu(\text{Zr}-\text{I})$ vibrations are not identified in the spectra of the complexes since they are expected to lie below the recording range of the instrument.

* Detailed IR spectral data of the adducts reported in this paper are available from the authors.

Thermal studies

The thermogravimetry of pyridine and substituted pyridine complexes with transition metal ions have been studied by Mazumdar et al. [15] and Allan et al. [16]. Little is known about the thermal properties of oxozirconium(IV) with nitrogen donor ligands [17]. For this reason thermogravimetric analyses of some of the representative complexes were also studied. The weight loss values observed in the thermal decomposition of oxozirconium(IV) complexes (Table 2) correspond very closely with the general equations



X = Cl; L = pic, 2,4 LN

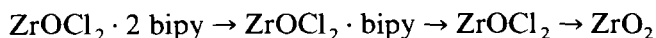
TABLE 2
Thermal data on oxozirconium(IV) complexes

Complex	Decompn. Temp	Decompn. product	TG wt. loss (%)	
			Found	Calcd.
ZrOCl ₂ ·4 (pic)	260	ZrOCl ₂ ·2 (pic)	34.31	33.81
	430	ZrOCl ₂	68.21	67.62
	570	ZrO ₂	79.01	77.60
ZrOCl ₂ ·4 (2,4 LN)	255	ZrOCl ₂ ·2 (2,4 LN)	36.01	35.30
	435	ZrOCl ₂	72.15	70.61
	560	ZrO ₂	80.06	79.67
ZrOCl ₂ ·2 (bipy)	210	ZrOCl ₂ ·bipy	32.38	31.82
	430	ZrOCl ₂	64.96	63.65
	550	ZrO ₂	76.35	74.85
ZrOBr ₂ ·4 (NH ₂ py)	245	ZrOBr ₂ ·2 (NH ₂ py)	30.56	29.23
	450	ZrOBr ₂	60.04	58.47
	560	ZrO ₂	82.10	80.83
ZrOBr ₂ ·4 (Q)	250	ZrOBr ₂ ·2 (Q)	34.96	32.94
	445	ZrOBr ₂	66.41	65.89
	555	ZrO ₂	85.92	84.26
ZrOBr ₂ ·4 (2,6 LN)	230	ZrOBr ₂ ·2 (2,6 LN)	31.92	30.78
	425	ZrOBr ₂	60.72	61.57
	550	ZrO ₂	84.03	82.27
ZrOI ₂ ·4 (NH ₂ py)·n H ₂ O	100	ZrOI ₂ ·4 (NH ₂ py)	5.7	
ZrOI ₂ ·4 (NH ₂ py)	240	ZrOI ₂ ·2 (NH ₂ py)	26.30	25.50
	430	ZrOI ₂	55.97	51.01
	550	ZrO ₂	85.39	83.28
ZrOI ₂ ·4 (pic)·x H ₂ O	100	ZrOI ₂ ·4 (pic)	6.30	
	245	ZrOI ₂ ·2 (pic)	26.31	25.37
	435	ZrOI ₂	54.36	50.74
	550	ZrO ₂	84.29	83.19

X = Br; L = NH₂py, Q, 2,6 LN

X = I; L = NH₂py, pic

and



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