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### INFRARED AND THERMAL STUDIES OF OXOZIRCONIUM(IV) COMPLEXES OF 4-CYANOPYRIDINE *N*-OXIDE

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Although coordination compounds of aromatic amine *N*-oxides with different metal salts have been extensively studied [1-3], comparatively little is known about the compounds of oxozirconium(IV) with aromatic amine *N*-oxides [4-16]. In the present communication we report our results on oxozirconium(IV) complexes of 4-cyanopyridine *N*-oxide (cypy).

#### EXPERIMENTAL

Lewis acids were obtained as reported previously [9,10,14], while the base 4-cyanopyridine *N*-oxide was obtained from Reilly Tar and Chemical Co., and was used as received. The metal complexes were prepared by the following general method. An ethanolic solution of Lewis acid was mixed with a slight excess of ligand. The reaction mixture was concentrated on a water bath, cooled, and an excess amount of diethyl ether was added. An oily viscous layer was obtained, which was separated and washed thoroughly with ether, dissolved in the minimum amount of absolute ethanol and again an excess of diethyl ether was added, from which a precipitate was obtained. The precipitate was filtered, washed with a small amount of ethanol and ether, and dried in vacuo over  $P_4O_{10}$ .

The selenocyanato complex was synthesised by the method already described for other selenocyanato complexes [14].  $ZrO(BPh_4)_2 \cdot 2cypy$  was prepared by mixing acetonic solutions of the metal salt and cypy and leaving the reaction mixture overnight. The crystalline complex separated out was washed with appropriate solvents and finally dried as previously described.

The analyses and other physical measurements of the complexes were made as reported earlier [10].

## RESULTS AND DISCUSSION

The analytical data are summarised in Table 1. The newly synthesised complexes are not hygroscopic in nature and are fairly stable at room temperature. The conductance measurements in  $\text{PhNO}_2$  indicate that halo, nitrate, thio- and selenocyanato, and tetraphenylboronato complexes are non-electrolytes, while the perchlorato complex dissociates in  $\text{PhNO}_2$  and behaves as a univalent electrolyte. The molecular weights of the compounds, as determined cryoscopically in freezing nitrobenzene, are in good agreement with the conductance values.

*Infrared spectral studies*

Table 1 records the significant IR bands of the ligand and its complexes. We recently reported the thorium(IV) complexes of cypyo [17]. A comparison of the IR spectra of the newly synthesised complexes with those of thorium(IV) and uranyl(VI) complexes [17,18] indicates that the N–O stretching vibration, which appears as a strong band at  $1265\text{ cm}^{-1}$  in the free ligand, suffers a significant negative shift ( $-\Delta\nu\text{NO} = 30\text{--}45\text{ cm}^{-1}$ ). This decrease in the frequency of the NO stretching vibration is attributed to coordination from the oxygen atom of the base causing a decrease in the  $\pi$ -character of the N–O bond [1–3]. The N–O bending vibration of the ligand assigned as a strong band at ca.  $840\text{ cm}^{-1}$  [1–3] suffers only a small shift in the oxozirconium(IV) complexes studied, which is in agreement with the earlier observations of Quagliano et al. [19,20]. Absorptions associated with the C–H out-of-plane deformation mode assigned at  $775\text{ cm}^{-1}$  are assumed to undergo a slight positive shift due to the tightening of the aromatic ring on complexation. A positive shift (ca.  $18\text{ cm}^{-1}$ ) has been observed in this mode of vibration [19,20]. In the far-IR region the medium or weak absorptions in the  $390\text{--}370\text{ cm}^{-1}$  region are assigned to  $\nu(\text{Zr–O})$  [6,15]. The Zr=O (oxocation) characteristic band is observed in all the complexes as a weak band in the  $980\text{--}920\text{ cm}^{-1}$  region [4–7].

In the perchlorato complex, the identification of two strong bands in the spectrum at  $1080\text{ cm}^{-1}$  ( $\nu_3$ ) and  $625\text{ cm}^{-1}$  ( $\nu_4$ ) suggests an ionic nature for both the perchlorate groups [4–6]. The absence of the  $\nu_3$  band of the ionic nitrate ( $D_{3h}$ ) around  $1360\text{ cm}^{-1}$  and the occurrence of two strong bands at  $1520$  and  $1300\text{ cm}^{-1}$  in the nitrate complex suggest the strong covalent nature of  $\text{NO}_3^-$  [21]. The bidentate nature of the nitrate groups is revealed by the presence of bands at  $1035$  ( $\nu_2$ ),  $820$  ( $\nu_6$ ) and  $735\text{ cm}^{-1}$  ( $\nu_3/\nu_5$ ) [22]. By applying the Lever separation method [23], a separation of ca.  $40\text{ cm}^{-1}$  in the combination bands ( $\nu_1 + \nu_4$ ) in the  $1800\text{--}1700\text{ cm}^{-1}$  region further confirms the bidentate nitrate coordination. Furthermore, the band associated with (Zr–O) (nitrate) is tentatively assigned at ca.  $225\text{ cm}^{-1}$  [18]. In the thio- and selenocyanato complexes, the intensity of the CN stretching band

TABLE 1  
Analytical and partial infrared data ( $\text{cm}^{-1}$ )<sup>a</sup> of oxozirconium(IV) complexes of 4-cyanopyridine *N*-oxide

Complex	Metal % found (calc.)	Nitrogen % found (calc.)	Carbon % found (calc.)	Hydrogen % found (calc.)	Anion % found (calc.)	$\nu(\text{N}-\text{O})$	$\nu(\text{Zr}=\text{O})$	$\nu(\text{Zr}-\text{O})$
ZrOCl <sub>2</sub> ·2cypyo	21.06 (21.77)	13.52 (13.39)	34.62 (34.44)	1.84 (1.91)	16.71 (16.98)	1220s	970w	390m
ZrOBr <sub>2</sub> ·2cypyo	17.12 (17.94)	11.42 (11.04)	28.62 (28.40)	1.51 (1.57)	31.21 (31.55)	1222s	960w	385m
ZrOI <sub>2</sub> ·2cypyo	14.82 (15.14)	9.62 (9.31)	24.12 (23.96)	1.51 (1.33)	41.52 (42.26)	1235s	—	370m
ZrO(ClO <sub>4</sub> ) <sub>2</sub> ·6cypyo	8.12 (8.86)	16.52 (16.37)	42.26 (42.10)	2.47 (2.33)	19.10 (19.39)	1225s	980w	380w
ZrO(NO <sub>3</sub> ) <sub>2</sub> ·2cypyo	19.82 (19.32)	17.56 (17.83)	30.72 (30.57)	1.75 (1.69)	—	1230s	970w	385m
ZrO(NCS) <sub>2</sub> ·2cypyo	19.96 (19.65)	18.29 (18.14)	36.42 (36.28)	1.79 (1.72)	24.62 (25.05)	1225s	940w	390m
ZrO(NCSe) <sub>2</sub> ·2cypyo	16.74 (16.33)	15.26 (15.08)	30.29 (30.16)	1.62 (1.43)	—	1230s	—	380m
ZrO(BPh <sub>4</sub> ) <sub>2</sub> ·2cypyo	9.41 (9.23)	5.82 (5.68)	73.16 (73.09)	5.01 (4.87)	—	1220s	920w	385m

<sup>a</sup> s = strong, m = medium, w = weak.

is useful in distinguishing the N- and X- (X = S or Se) bonded complexes [14,24]. The  $\nu(\text{CN})$ ,  $\nu(\text{CX})$  and  $\delta(\text{NCX})$  in both the complexes occur at ca. 2080, 680 and 430  $\text{cm}^{-1}$ , respectively, thus indicating the N-bonded NCS or NCSe group. The IR spectrum of  $\text{ZrO}(\text{BPh}_4)_2 \cdot 2\text{cypyo}$  shows the four medium or strong bands at ca. 1480, 1445, 1430 and 1395  $\text{cm}^{-1}$ , which indicate the presence of tetraphenyl boronate coordinated to a metal ion through a  $\pi$ -bond of the phenyl ring [9,25].

### Thermal studies

Thermal investigations of the oxozirconium(IV) complexes of aromatic amine *N*-oxides have been limited [4,5,8,10,15,16]. In the present paper, chloro, bromo, thiocyanato, perchlorato and nitrate complexes have been studied. The thermal behaviour of thorium(IV) complexes of cypyo have already been investigated [17]. The results of thermal analyses are given in Table 2. Similar to Th(IV) complexes, the TG and DTG curves of oxozirconium(IV) complexes of cypyo indicate that the compounds have no water of crystallisation and are non-hygroscopic in nature. The low-temperature decomposition of the iodo complex (ca. 120°C) indicates the presence of loosely held iodo ligands. Even when the compound is kept enclosed for a long time, violet iodine vapours accumulate, indicating the lower stability of this complex. Other halo and nitrate complexes decompose endothermally, while the perchlorato complex decomposes exothermally with explosion and the evolution of smoke [26]. The TG curves show that halo and nitrate

TABLE 2

Thermal decomposition data for ZrO(IV) complexes of 4-cyanopyridine *N*-oxide in air

Compound	Decomposition temp. (°C)		Decomposition product	TG wt. loss (%)		DTG temp. (°C) & peak
	Initial	Final		Found	Calc.	
	ZrOCl <sub>2</sub> ·2cypyo	210		420	ZrOCl <sub>2</sub>	
	480	590	ZrO <sub>2</sub>	73.17	70.57	450 exo
ZrOBr <sub>2</sub> ·2cypyo	205	425	ZrOBr <sub>2</sub>	49.23	47.33	270 endo
	490	590	ZrO <sub>2</sub>	77.16	75.73	430 exo
ZrO(NO <sub>3</sub> ) <sub>2</sub> ·2 cypyo	215	425	ZrO(NO <sub>3</sub> ) <sub>2</sub>	52.61	50.95	290 endo
	480	600	ZrO <sub>2</sub>	75.46	73.88	450 exo
ZrO(ClO <sub>4</sub> ) <sub>2</sub> · 6cypyo	190	370	ZrO(ClO <sub>4</sub> ) <sub>2</sub> · 4cypyo	24.51	23.39	210 exo
	390	500	ZrO(ClO <sub>4</sub> ) <sub>2</sub>	72.16	70.17	430 exo
	510	610	ZrO <sub>2</sub>	89.91	88.01	-
ZrO(NO <sub>3</sub> ) <sub>2</sub> · 2cypyo	215	425	ZrO(NO <sub>3</sub> ) <sub>2</sub>	52.16	50.95	215 endo
	480	600	ZrO <sub>2</sub>	75.86	73.88	440 exo

complexes complete their thermal processes in two steps. In the first step, both ligand molecules are lost and, in the second step  $ZrO_2$  is finally formed as end product. No stable intermediate complex has been isolated in these cases. A survey of the TG curves of  $ZrO(ClO_4)_2 \cdot 6cypyo$  indicates that two ligand molecules are lost at ca. 275°C and a stable complex,  $ZrO(ClO_4)_2 \cdot 4cypyo$ , is isolable at this temperature. Further heating of the sample to 390°C causes the removal of the remaining ligands and finally, at 620°C, metal oxide is formed.

In conclusion, the order of stability of the complexes is:  $I < ClO_4 < NCS < Br < Cl < NO_3$ .

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