Note

INFRARED AND THERMAL INVESTIGATIONS OF OXOZIRCONIUM(IV) CHELATES OF 1,10-PHENANTHROLINE N-N'-DIOXIDE

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The donor properties of various aromatic amine N-oxides with different metal salts have been studied extensively [1–3]; oxozirconium(IV) complexes of pyridine N-oxide [4,5], quinoline N-oxide [6], 2,6-lutidine N-oxide [5], 2-methyl pyridine N-oxide [7], 2,2'-bipyridine mono N-oxide [8], 2,2'-bipyridine N-N'-dioxide [9,10], 1,10-phenanthroline mono N-oxide [11] and 2-ethoxy carbonyl amino pyridine N-oxide [12] are known. In the present communication, we report the synthesis, infrared and thermal behaviour of chelates of oxozirconium(IV) salts with 1,10-phenanthroline N-N'-dioxide (PhenO$_2$). Vanadium(IV), [13], thorium(IV) [14], dioxouranium [14] and some rare earth nitrates [15] chelates of this ligand have already been studied.

EXPERIMENTAL

The ligand was prepared by the method described for 2,2'-bipyridyl N-N'-dioxide [16,17]. All the compounds were prepared by adopting the following general method. To a hot solution of the metal salt in methanol a sufficient amount of 2,2'-dimethoxy propane was added for dehydration. This solution was mixed with a stoichiometric amount of the ligand in the same solvent. The reaction mixture was refluxed for about 2 h and the excess solvent was removed by distillation

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RESULTS AND DISCUSSION

The analytical data of the newly synthesised chelates are summarised in Table 1. The chelates are insoluble in common organic solvents but soluble in coordinating solvents such as DMSO or DMF. The conductance measurements in these solvents indicate that chloro, bromo, nitrato and thiocyanato complexes are non-electrolytes, while perchlorato and iodo complexes dissociate in these solvents and behave as uni-bivalent electrolytes. The molecular weight could not be determined due to insolubility of these compounds in benzene or nitrobenzene.

Infrared spectral studies

Table 1 records important IR bands for the ligand and the chelates. The assignments are largely based on previous work on this ligand [13–15] and on the spectrum of 2,2'-bipyridine N-N'-dioxide [18]. In the IR spectrum of the free ligand two $\nu(N–O)$ bands have been observed at 1312 and 1282 cm^{-1}. These bands have been observed to shift to lower frequencies upon complexation. The decrease in the frequency of the $\nu(N–O)$ vibration is attributed to O, O-chelation in PhenO$_2$ [13–15]. Absorptions of strong intensities in the region 880–845 cm^{-1} have been assigned to the N–O

TABLE 1

Analytical, conductivity and spectral data for oxozirconium (IV) chelates

Complex	% Metal found (calcd.)	% Nitrogen found (calcd.)	% Anion found (calcd.)	Conductivity (Ω^{-1} cm^{-1} mol^{-1})	$\nu(N–O)$ (cm^{-1})	$\nu(Zr–O)$ (cm^{-1})
PhenO$_2$					1312s 1282s	
ZrOCl$_2$·PhenO$_2$	23.54 (23.33)	7.18 (7.17)	18.26 (18.20)	10.7 [a] 14.9 [b]	1280s 1265m	405m
ZrOBr$_2$·PhenO$_2$	19.14 (18.99)	5.92 (5.84)	33.46 (33.40)	14.9 [a] 20.1 [b]	1290m 1270m	400m
ZrOI$_2$·2PhenO$_2$	11.61 (11.59)	7.16 (7.13)	32.46 (32.35)	80.1 [a] 157.9 [b]	1290m 1280sh	410m
ZrO(ClO$_4$)·3PhenO$_2$	9.72 (9.66)	8.98 (8.91)	21.24 (21.12)	86.6 [a] 163.9 [b]	1270s 1260m	375m 370sh
ZrO(NO$_3$)$_2$·PhenO$_2$	20.62 (20.54)	12.72 (12.64)		9.2 [a] 17.2 [b]	1280m 1270sh	370sh 365m
ZrO(NCS)$_2$·PhenO$_2$	21.00 (20.91)	12.92 (12.87)	26.76 (26.66)	10.9 [a] 17.3 [b]	1290m 1275m	395m

[a] In DMSO.
[b] In DMF.

bending mode and from the tabulated data, it appears that only a slight shift of this frequency is observed on complexation; further support for the O,O-chelation. A positive shift has been observed in the vibrations associated with C–H out of plane deformation, which is due to tightening of the aromatic ring on complexation [1–3]. In the far IR region, metal–ligand vibrations have been identified. The overall IR spectral evidence suggests that PhenO$_2$ acts as a bidentate O,O-chelating agent forming a seven membered chelate ring with ZrO^{2+}.

The Zr=O double bond characteristic frequency appears in all the compounds in the region 990–940 cm^{-1} [9,11,15].

The strong absorptions at 1080 cm^{-1} (ν_3) and 620 cm^{-1} (ν_4) in the perchlorato complex due to perchlorate ions, indicate that the Td symmetry has not been disturbed and that not all the perchlorate ions are bonded to the zirconium ion [4,9,15]. In the nitrato complex the absence of a band at 1360 cm^{-1} (ν_3 band of ionic nitrate D_{3h}) and the presence of two strong bands at 1510 and 1300 cm^{-1} indicate the covalent nature of nitrate groups in the complex [19]. The bidentate nature of the nitrato groups is revealed by the presence of other bands at 1035 (ν_2), 820 (ν_6) and 735 (ν_3/ν_5) [20]. The separation (40 cm^{-1}) in combination bands ($\nu_1 + \nu_4$) (1740 and 1700 cm^{-1}) further confirms bidentate nitrato coordination [21]. Furthermore, the band associated with ν(Zr–O) (nitrato) is tentatively assigned at 235 cm^{-1} [22]. In the thiocyanato complex the presence of bands at 2055 (νC≡N), 840 (νC–S) and 460 cm^{-1} (δNCS) indicates the N-bonded terminal isothiocyanate to metal ion [23]. The N-bonding is further proven by ν(Zr–N) absorption (tentatively assigned) at 270 cm^{-1} [24].

In conclusion, the coordination number of zirconium(IV) in these chelates is five or seven depending upon the anions.

THERMAL STUDIES

Recently we have described [25] the thermal properties of complexes of oxozirconium(IV) with various aromatic amine N-oxides viz., pyridine N-oxide, 2,6-lutidine N-oxide and 1,10-phenanthroline mono N-oxide. It would be interesting to study the thermal properties of oxozirconium(IV) chelates with 1,10-phenanthroline N-N'-dioxide and compare them with the existing thermal studies with different amine N-oxides.

The thermal behaviour of this ligand with thorium(IV) and dioxouranium(VI) have already been investigated [15]. The results of thermal analyses are summarized in Table 2. The TG and DTG curves of the present chelates show the absence of water molecules either in or out of the coordination sphere and that the chelates degrade to the metal oxide in air over the temperature range 190–625°C. Agreement between experimental and theoretical mass losses is within experimental error ($\pm 2.0\%$) in all cases.

TABLE 2

Thermogravimetric analysis data in air

Compound	Decomposition temp. (°C)		Decomposition product	TG loss (wt. %)		DTG peak
	Initial	Final		Found	(calcd)	
$ZrOCl_2 \cdot PhenO_2$	190	310	$ZrOCl_2$	53.19	(54.35)	endo
	530	620	ZrO_2	66.59	(68.46)	
$ZrOBr_2 \cdot PhenO_2$	230	315	$ZrOBr_2$	45.21	(44.25)	endo
	535	625	ZrO_2	75.61	(74.32)	
$ZrO(NCS)_2 \cdot PhenO_2$	220	310	$ZrO(NCS)_2$	47.90	(48.73)	endo
	530	615	ZrO_2	70.93	(71.72)	
$ZrO(NO_3)_2 \cdot PhenO_2$	250	330	$ZrO(NO_3)_2$	46.12	(47.85)	endo
	540	620	ZrO_2	70.10	(72.23)	
$ZrO(ClO_4)_2 \cdot 3PhenO_2$	230	300	$ZrO(ClO_4) \cdot 2PhenO_2$	21.23	(22.50)	
	305	340	$ZrO(ClO_4)_2$	69.42	(67.51)	exo
	550	625	ZrO_2	88.29	(86.94)	

The TG curves show essentially two stage processes for chloro, bromo, thiocyanato and nitrato chelates. Stepped mass losses for $ZrOX_2 \cdot PhenO_2$ ($X = Cl$, Br, NCS or NO_3) suggest that heterocyclic N-oxide ligand is lost initially (190–340°C) and the final stage involves the formation of ZrO_2. In addition, the fine detail from the DTG curves show that these chelates decompose endothermically within the temperature region.

In contrast to this behaviour $ZrO(ClO_4)_2 \cdot 3PhenO_2$ initially (230–300°C) loses one ligand molecule and a stable intermediate compound $ZrO(ClO_4)_2 \cdot PhenO_2$ is obtained. A further increase in temperature up to 340°C causes the removal of remaining ligands and finally, at 625°C, ZrO_2 is obtained as the end product. The DTG curves show one sharp exo peak not seen before. The thermal reaction is violent, with formation of smoke due to the oxygen content of the perchlorate [26].

In conclusion, the decomposition temperature varies from ligand to ligand. If the minimum TGA decomposition temperature is taken as a rough criterion of thermal stability, then the order for ZrO(IV) complexes with different amine N-oxides (cf. ref. 25) is

PhenO > PhenO$_2$ > LNO > PyO
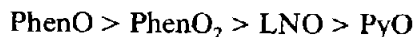
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