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Note

INFRARED AND THERMAL INVESTIGATIONS OF OXOZIRCONIUM(IV) COMPLEXES OF 2-METHYL AMINO PYRIDINE *N*-OXIDE

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The ligational behaviour of 2-amino pyridine *N*-oxide was first studied by Katritzky [1] and Sigel and Brintzinger [2]. It has two potential donor sites in the *N*-oxygen and 2-amino groups. Thus, as the neutral molecule, this ligand acts as a monodentate, while the loss of a proton from the 2-amino group leads to stable complexes containing a bidentate ligand with Fe(III) and Cu(II) [2]. A similar behaviour has been shown by the related ligand 2-methyl amino pyridine *N*-oxide (MAPO), in which it can behave as either a monodentate or bidentate ligand with metal ions [3,4]. Thus, it was considered worthwhile to study the oxozirconium(IV) complexes of this ligand.

EXPERIMENTAL

The ligand MAPO was prepared by the method of Katritzky [5]. Lewis acids were obtained as reported earlier [6]. All the complexes were prepared by the following general method. To hot methanolic solutions of oxozirconium(IV) salts a sufficient amount of 2,2′-dimethoxy propane was added for dehydration. This solution was mixed with a stoichiometric amount of the ligand and refluxed for about 1 h. The excess solvent was removed by distillation. The residual mass, on treatment with anhydrous ether, yielded a crystalline solid which was filtered, washed with diethyl ether and dried in vacuo over anhydrous $CaCl_2$.

The analyses and physical measurements of the complexes were made as reported earlier [6].

RESULTS AND DISCUSSION

The analytical data of the newly synthesised complexes are summarised in Table 1. The complexes are insoluble in common organic solvents but

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soluble in coordinating solvents such as DMSO or DMF. Conductance measurements in these solvents indicate that the chloro, bromo, nitrato and thiocyanato complexes are non-electrolytes, while the perchlorato and iodo complexes dissociate in these solvents and behave as uni–bivalent electrolytes. Molecular weights could not be determined due to the insolubility of these compounds in benzene or nitrobenzene.

Infrared spectral studies

Table 1 records the important IR bands for the ligand and complexes studied. The assignments are largely based on previous work on this ligand [3,4] and other related amine *N*-oxide complexes of oxozirconium [7]. In the IR spectrum of the free ligand, the ν(N–O) band was observed at 1205 cm^{-1} as a strong absorption. In all the complexes studied, the position of the N–O stretching frequency is shifted to lower wavenumbers. The decrease in the N–O stretching vibration is attributed to coordination from the oxygen atom of the base causing a decrease in π-character of the N–O bond [6,7]. The δ(NO) mode in the pure ligand is also at a somewhat lower frequency than that observed for most pyridine *N*-oxides. This band, because of two opposing effects [8], is often not significantly shifted upon complexation, which is the case for this series of complexes.

Because of the intramolecular hydrogen bonding in the pure ligand, it is difficult to determine whether there is any bidentate formation, i.e., additional bonding by the amine nitrogen in these complexes. However, a comparison of the ν(N–H), δ(N–H), $N{-}CH_3$ deformation and ν(C–N) of these complexes does not indicate bonding between the amine nitrogen and the metal ion. The nature of the oxocation in these complexes is not certain. However, a weak band in the 970–950 cm^{-1} region in these complexes has been assigned as the Zr=O double bond stretching frequency [7,8]. The M–O stretching frequency in these complexes has been assigned to the 415–350 cm^{-1} region [7,8].

In the perchlorato complex the very strong ν_3 band and a strong ν_4 band appear at ca. 1080 and 625 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 [9,10]. The absence of the ν_3 band of ionic nitrate D_{3h} around 1360 cm^{-1} and the occurrence of two strong bands at ca. 1520 (ν_4) and 1310 cm^{-1} (ν_1) in the spectrum of $ZrO(NO_3)_2 \cdot 2MAPO$ suggest the coordination of nitrate ions in this complex [11,12]. The two combination bands ($\nu_1 + \nu_4$) appeared as weak bands at ca. 1760 and 1720 cm^{-1} in the spectra. By applying the Lever separation method [13], the separation of 40 cm^{-1} in this case suggests a bidentate nature of the nitrato groups. The presence of bands at ca. 1030 (ν_2), 810 (ν_6) and 740 cm^{-1} (ν_3/ν_5) further confirms the bidentate nature of the nitrate groups [14]. The IR spectra of the thio- and selenocyanato complexes show bands at ca. 2050

TABLE 1
Analytical, conductivity and infrared spectral (cm^{-1}) data (values in DMSO)

Compound	Found (Calcd.)(%)			Λ_m ($ohm^{-1}cm^{-2}$ mol^{-1})	ν(NH)	δ(N–H)	ν(CN)	ν(NO)	ν(M–O)
	Zr	N	Anion						
$C_6H_8N_2O$	–	–	–	–	3350m,b	1615w	1250(s)	1205(s)	–
$ZrOCl_2 \cdot 2C_6H_8N_2O$	20.96 (21.36)	12.94 (13.14)	16.21 (16.66)	10.3	3360m,b	1620w	1260m	1190s	415m
$ZrOBr_2 \cdot 2C_6H_8N_2O$	17.32 (17.66)	10.69 (10.87)	30.79 (31.06)	11.4	3355m,b	1618w	1265m	1192s	390m
$ZrOI_2 \cdot 4C_6H_8N_2O$	10.31 (10.61)	12.86 (13.06)	29.32 (29.63)	80.7	3350m,b	1622w	1263m	1185s	350m
$ZrO(ClO_4)_2 \cdot 6C_6H_8N_2O$	8.32 (8.66)	15.81 (16.00)	18.49 (18.95)	78.9	3352m,br	1620w	1261m	1182s	360m
$ZrO(NO_3)_2 \cdot 2C_6H_8N_2O$	18.62 (18.99)	17.36 (17.53)	–	9.9	3360m,br	1619w	1262m	1180s	410m
$ZrO(NCS)_2 \cdot 2C_6H_8N_2O$	19.06 (19.32)	17.52 (17.83)	24.32 (24.62)	10.9	3358m,br	1621w	1265m	1180s	400m
$ZrO(NCSe)_2 \cdot 2C_6H_8N_2O$	15.82 (16.10)	14.57 (14.86)	–	11.2	3355m,br	1622w	1263m	1182s	390m
$ZrO(BPh_4)_2 \cdot 2C_6H_8N_2O$	8.86 (9.16)	5.42 (5.63)	–	9.7	3350m,br	1620w	1261m	1180s	395m

ν(CN), 780 ν(C–X) and 480 cm^{-1} δ(NCX) (X = S or Se), which are attributed to the N-bonded NCS and NCSe groups [15,16]. On comparing the IR spectrum of $ZrO(BPh_4)_2 \cdot 2MAPO$ with that of sodium tetraphenylboron [17,18] in the 1500–1350 cm^{-1} region, it is found that the IR spectrum of the tetraphenylboronato complex has four strong bands at 1480, 1455, 1430 and 1385 cm^{-1} which conclusively indicate the coordination of tetraphenylboronato to the zirconium(IV) ion through the π-bond of a phenyl ring [17,18].

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

THERMAL STUDIES

Thermal investigations of oxozirconium(IV) complexes with various aromatic amine *N*-oxides, viz. 2,2′-bipyridyl *N,N*′-dioxide [19] 2-methyl pyridine *N*-oxide [6], pyridine *N*-oxide [20], 2,6-lutidine *N*-oxide [20], 1,10-phenanthroline *N,N*′-dioxide [7] and 4-cyanopyridine *N*-oxide [21], have already been reported. In the present work, the thermal studies with regard to some oxozirconium(IV) complexes of MAPO and their intermediates are reported.

The results of thermal analyses are summarised in Table 2. The TG and DTG curves of oxozirconium(IV) complexes of MAPO indicate that the compounds have no water of crystallization and are non-hygroscopic in nature. The halo and nitrato complexes decompose endothermally, while the perchlorato complex decomposes exothermally with a slight explosion and the evolution of smoke. Analysis of the TG curves shows that the compound decomposed into ZrO_2 in air over the temperature range 210–540°C. The

TABLE 2
Thermal data on oxozirconium(IV) complexes of MAPO

Complex	Decomposition temp. (°C)		Decomposition product	TG loss (wt.%)		DTG peak (°C)
	Initial	Final		Found	(Calcd.)	
$ZrOCl_2 \cdot 2C_6H_8N_2O$	220	390	$ZrOCl_2$	59.26	(58.21)	290 endo
	430	540	ZrO_2	72.89	(71.12)	500 exo
$ZrOBr_2 \cdot 2C_6H_8N_2O$	215	380	$ZrOBr_2$	49.36	(48.15)	280 endo
	425	540	ZrO_2	77.81	(76.11)	490 exo
$ZrO(ClO_4)_2 \cdot 6C_6H_8N_2O$	210	395	$ZrO(ClO_4)_2$	72.11	(70.85)	310 exo
	430	535	ZrO_2	90.06	(88.28)	490 exo
$ZrO(NO_3)_2 \cdot 2C_6H_8N_2O$	230	390	$ZrO(NO_3)_2$	52.01	(51.77)	315 endo
	430	540	ZrO_2	75.16	(74.32)	495 exo
$ZrO(NCS)_2 \cdot 2C_6H_8N_2O$	215	390	$ZrO(NCS)_2$	53.82	(52.65)	320 endo
	425	540	ZrO_2	75.16	(73.88)	490 exo

experimental error was ±2% in all cases studied. A comparison of previous thermal studies with different aromatic amine *N*-oxides [6,20,21] indicates that the chelates of amine *N*-oxides are more stable than the complexes. The thermal stability of the different amine *N*-oxides may fall in the following order: PhenO > $PhenO_2 \approx BipyO_2$ > MAPO > PicO > LNO > PyO.

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