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Compounds of Oxozirconium(IV) Alkoxides With Oxygen and Nitrogen Bases

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Pyridine, quinoline, 2,2′-bipyridyl, dimethylformamide, dimethylacetamide and phthalimide combine with $ZrOCl(OCHMe_2)\cdot 2\,Me_2CHOH$ to form complexes, $ZrOCl(OCHMe_2)\cdot$Base [with the exception of dimethylsulfoxide: $Zr_2O_2Cl_2(OCHMe_2)_2\cdot 3\,DMSO$], whereas dialkoxides, $ZrO(OR)_2\cdot ROH$ ($R = Me, Et, Pr^i$), fail to react. The complexes have been characterized through infrared, molar conductance and thermal decomposition studies.

[Keywords: Oxozirconium(IV) alkoxide compounds; Zirconium complexes]

Komplexe von Oxozirkonium(IV)-Alkoxiden mit Sauerstoff- und Stickstoff-Basen

Pyridin, Chinolin, 2,2′-Bipyridyl, Dimethylformamid, Dimethylacetamid und Phthalimid geben mit $ZrOCl(OCHMe_2)\cdot 2\,Me_2CHOH$ Komplexe vom Typ $ZrOCl(OCHMe_2)\cdot$Base [ausgenommen *DMSO*: $Zr_2O_2Cl_2(OCHMe_2)_2\cdot 3\,DMSO$], während Dialkoxide, $ZrO(OR)_2\cdot ROH$ ($R = Me, Et, Isopr$), keine Reaktion ergeben. Die Komplexe wurden durch ihre IR-Spektren, molare Leitfähigkeit und mittels Untersuchung der thermischen Zersetzung charakterisiert.

Introduction

Oxozirconium(IV) alkoxides of the types $ZrO(OR)_2\cdot ROH$ and $ZrOCl(OR)\cdot 2\,ROH$, where $R = Me$, Et and Pr^i, have recently been synthesised[1]. The work presented in this paper was undertaken to compare the acceptor behaviour of completely substituted and the monochloro derivatives towards strong nitrogen and oxygen bases and to isolate and characterize their complexes.

Experimental

Physical measurements and elemental analyses were done as already reported[1].

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Table 1. *Melting point, molar conductance (25°; in nitrobenzene) and elemental analysis of oxozirconium(IV) complexes*

Compound	mp (°C) (decomp.)	mol. conductance ($cm^2\,\Omega^{-1}\,mol^{-1}$)	Elemental Zr	Analysis Cl	N	Found (Calc.) % C	H
$ZrOCl(OCHMe_2) \cdot C_5H_5N$ (**1**)	125	0.9	32.4 (32.5)	12.2 (12.6)	4.6 (5.0)	33.8 (34.2)	4.2 (4.3)
$ZrOCl(OCHMe_2) \cdot C_9H_7N$ (**2**)	116	1.0	27.5 (27.6)	10.3 (10.7)	4.2 (4.2)	42.6 (43.5)	4.2 (4.2)
$ZrOCl(OCHMe_2) \cdot$ *bipy* (**3**)	107	1.7	24.8 (25.2)	10.0 (9.8)	7.4 (7.7)	43.0 (43.1)	4.0 (4.1)
$ZrOCl(OCHMe_2) \cdot$ *DMF* (**4**)	96	0.5	33.0 (33.2)	12.4 (12.9)	5.2 (5.1)	25.9 (26.1)	4.8 (5.1)
$ZrOCl(OCHMe_2) \cdot$ *DMA* (**5**)	109	1.0	30.5 (31.6)	11.9 (12.3)	5.0 (4.9)	24.2 (24.9)	5.2 (5.5)
$Zr_2O_2Cl_2(OCHMe_2)_2 \cdot 3$ *DMSO* (**6**)	76	0.4	28.4 (28.6)	10.9 (11.1)	—	22.2 (22.6)	5.1 (5.0)
$ZrOCl(OCHMe_2) \cdot$ *phth* (**7**)	>200	1.3	26.0 (26.1)	10.1 (10.2)	3.9 (4.0)	36.8 (37.9)	3.2 (3.4)

Table 2. *Important ir bands (cm^{-1}) of oxozirconium(IV) complexes*

Compound	Ligand vibrations[a] (Assignments)	νCO	νZr $\underline{\leftarrow}$ O	νZr—O→	νZr—Cl	νZr ← L[b]
1	1640 sh, 1590 s, 1540 m, 1455 m (νC=C, νC=N) 630 s (605 s), 430 m (405 s), (Amine ring vib.)	1050 w, 1035 m	655 s	530 m, 470 m, 280 s	395 w, 305 s	290 m
2	1640 sh, 1595 s, 1540 s, (νC=C, νC=N) 670 m (615 m), 515 m (480 m), (Amine ring vib.)	1050 w, 1030 m	650 sb	530 w, 470 m, 280 s	390 w, 305 s	292 m
3	1595 m, 1580 s, 1570 m, 1550 m (Ring vib.)	1022 s	652 s	532 m, 460 s, 285 m	392 m, 305 s	310 s
4	1650 s (1670 sb), ν(C=O)	1045 w, 1030 m	650 s	528 m, 460 s, 290 m	380 s, 305 m	368 s
5	1605 s (1660 s), ν(C=O)	1025 s	652 s	530 m, 470 s, 280 m	380 sh, 310 s	370 s
6	950 s (1053 s), ν(S=O); 723 m (697 m), ν(C—S)	1030 s	650 sb	528 m, 470 m, 280 s	390 w, 305 s	440 m
7	3380 sh, 3185 mb (3180 s), ν(N—H); 1778 m, 1740 s (1770 s, 1740 s), 1700 s, ν(C=O)	1055 m, 1030 m	655 s	532 m, 480 m, 282 m	390 m, 310 s	360 w

[a] Bands in parentheses refer to pure ligands.

[b] L refers to nitrogen or oxygen donor atoms.

All addition complexes were prepared and handled on a vacuum line and under an atmosphere of dry nitrogen. A known weight of the alkoxide, $\mathrm{ZrOCl(OCH}Me_2) \cdot 2\,Me_2\mathrm{CHOH}$ was dissolved in methylene chloride and the base, neat or in solution, was added dropwise. The reaction mixture was stirred for ca. 12 h and the contents were evacuated in all cases except phthalimide where the mixture was filtered and the filtrate was evacuated. The residue was stirred with $\mathrm{CCl_4}$, petroleum ether or ether, filtered and the solid was washed thoroughly and then dried under vacuum (10^{-4} torr).

Analytical data, melting point and molar conductance are given in Table 1, while some important ir bands are summarized in Table 2.

Results and Discussion

The dialkoxides, $\mathrm{ZrO(O}R)_2 \cdot R\mathrm{OH}$ ($R = Me$, Et, Pr^i) appear to be high polymers and do not get desolvated even on heating under high vacuum. Treatment with strong bases does not cause alcohol replacement and no adducts with bases are formed. This implies that alcohol molecules are very strongly held in the polymeric chain of oxozirconium(IV) and the metal appears to be coordinatively saturated through alkoxy and oxo bridges. The chloroalkoxyoxozirconium(IV) compounds, $\mathrm{ZrOCl(O}R) \cdot 2\,R\mathrm{OH}$, on the other hand, are comparatively less associated, probably due to the electron attracting chloro group on metal, and form addition complexes when treated with bases stronger than ROH. In the process ROH gets eliminated. Important ir bands of the complexes are given in Table 2 and only a few have been discussed in the text.

Tertiary nitrogen bases (B), pyridine and quinoline combine with $\mathrm{ZrOCl(OCH}Me_2) \cdot 2\,Me_2\mathrm{CHOH}$ to form complexes, $\mathrm{ZrOCl(OCH}Me_2) \cdot B$. Coordination of tertiary bases[2–4] results in a slight upward shift of some $\nu\mathrm{C{=}C}$ and $\nu\mathrm{C{=}N}$ modes observed between 1615-1450 cm^{-1}. Another significant change involves a shift to higher frequency of the amine ring vibration on coordination (Table 2). A new band appearing at 290 cm^{-1} has been assigned by comparison[5] to $\nu\mathrm{Zr \leftarrow N}$. The bidentate base, 2,2′-bipyridyl, (*bipy*), forms an adduct, $\mathrm{ZrOCl(OCH}Me_2) \cdot (bipy)$, whose ir is consistent with analogous complexes of *bipy* with metal halides[6]. A new band, characteristic for chelated ligand[6], appears at 1320 cm^{-1}. Furthermore, the *bipy* band at 402 cm^{-1} shifts to 420 cm^{-1} in the complex as a consequence of chelation[6]. A band at 310 cm^{-1} has tentatively been assigned to $\nu\mathrm{Zr \leftarrow N}$.

The amides (A), dimethylformamide (DMF) and dimethylacetamide (DMA) form addition complexes of composition, $\mathrm{ZrOCl(OCH}Me_2) \cdot A$. Band formation between an amide molecule and the metal ion generally occurs through carbonyl oxygen[7] and this results in a lowering of ν C = O. A lowering of the order of 20-50 cm^{-1} in ν C = O has been observed in these complexes (Table 2). New bands appearing around 370 cm^{-1} may be assigned to the stretching mode of metal—amide oxygen, Zr ← O. Dimethylsulphoxide, *DMSO*, on the

Scheme 1

1:

$$[ZrOCl(OCH\mathit{Me}_2)\cdot C_5H_5N]_4 \xrightarrow[-2(C_3H_6)]{60-120^\circ} Zr_4O_4Cl_4(OH)_2(OCH\mathit{Me}_2)_2\cdot 4\,C_5H_5N \xrightarrow[-2C_5H_5N,\ -(C_3H_6)]{120-200^\circ} Zr_4O_4Cl_4(OH)_3(OCH\mathit{Me}_2)\cdot 2\,C_5H_5N$$

$$\xrightarrow[-2C_5H_5N,\ -(C_3H_6)]{200-320^\circ} [ZrO(OH)Cl]_4 \xrightarrow[-4HCl]{320-540^\circ} 4\,ZrO_2$$

2:

$$[ZrOCl(OCH\mathit{Me}_2)\cdot C_9H_7N]_4 \xrightarrow[-2(C_3H_6),\ -4(C_9H_7N)]{70-280^\circ} Zr_4O_4Cl_4(OH)_2(OCH\mathit{Me}_2)_2 \xrightarrow[-2(C_3H_6),\ -HCl]{280-340^\circ} Zr_4O_5(OH)_3Cl_3 \xrightarrow[-3HCl\ (2\ steps)]{340-520^\circ} 4\,ZrO_2$$

3:

$$[ZrOCl(OCH\mathit{Me}_2)\cdot \mathit{bipy}]_4 \xrightarrow[-2(C_3H_6)]{60-130^\circ} Zr_4O_4Cl_4(OH)_2(OCH\mathit{Me}_2)_2\cdot 4\,\mathit{bipy} \xrightarrow[-2(C_3H_6),\ -3\,\mathit{bipy}]{130-320^\circ} Zr_4O_4Cl_4(OH)_4\cdot \mathit{bipy}$$

$$\xrightarrow[-\mathit{bipy},\ -2HCl]{320-440^\circ} Zr_4O_6Cl_2(OH)_2 \xrightarrow[-2HCl]{440-540^\circ} 4ZrO_2$$

4, 5:

$$[ZrOCl(OCH\mathit{Me}_2)\cdot A]_4 \xrightarrow[-4(C_3H_6),\ -2\,A]{60-220^\circ} Zr_4O_4Cl_4(OH)_4\cdot 2\,A \xrightarrow[-A]{220-280^\circ} Zr_4O_4Cl_4(OH)_4\cdot A \xrightarrow[-A,\ -4HCl\ (2steps)]{280-520^\circ} 4\,ZrO_2$$

(where A = *DMF, DMA*)

6:

$$Zr_4O_4Cl_4(OCH\mathit{Me}_2)_4\cdot 6\,\mathit{DMSO} \xrightarrow[-2(C_3H_6)]{60-150^\circ} Zr_4O_4Cl_4(OH)_2(OCH\mathit{Me}_2)_2\cdot 6\,\mathit{DMSO} \xrightarrow[-2(C_3H_6),\ -5\,\mathit{DMSO}]{150-280^\circ} Zr_4O_4Cl_4(OH)_4\cdot \mathit{DMSO}$$

$$\xrightarrow[-\mathit{DMSO},\ -4HCl\ (2\ steps)]{280-540^\circ} 4ZrO_2$$

other hand, provides a complex, $Zr_2O_2Cl_2(OCH\mathit{Me}_2)_2\cdot 3\,\mathit{DMSO}$. It shows ir bands typical of coordinated *DMSO* characterised[8] by a shift to a lower frequency region of the ν S = O from 1053 in pure *DMSO* to 950 cm^{-1} in the complex and the upward shift of the C—S vibration from 697 in ligand to 723 cm^{-1} in its complex. The metal oxygen stretching mode arising as a result has been tentatively attributed at 440 cm^{-1}.

Imides may undergo substitution as well as addition both separately and simultaneously. No substitution takes place inspite of heating with phthalimide (*phth*) and the compound corresponds to composition, $\mathrm{ZrOCl(OCH}Me_2\mathrm{)} \cdot (phth)$. As evidenced by ir (Table 2) the ligand behaves as a monodentate and furthermore only one carbonyl group per ligand molecule coordinates to the metal atom[9] (Table 2). Also, almost no lowering is observed in the ν NH vibration (Table 2). A new band at 360 cm^{-1} is tentatively assigned to $\nu \mathrm{Zr} \leftarrow \mathrm{O}$.

The addition complexes, like the parent alkoxide, are expected to contain bridged alkoxy groups. The bands at ca. 500, 450 and 280 cm^{-1} are probably due to vibrations involving $\mathrm{Zr—O} \rightarrow$ bonds. Bands located at ca. 380 and 305 cm^{-1} in adducts (like in the parent alkoxides[1]) refer probably to $\nu \mathrm{Zr—Cl}$ (Table 2). These compounds do not contain any sharp intensity bands in the range 800—1000 cm^{-1} or broad intense bands in 700-900 cm^{-1} thus ruling out any isolated $\mathrm{Zr}=\mathrm{O}$ bonds and metal—oxygen chains containing bonds of higher multiplicity[10]. The presence of fairly intense narrow bands at 650-660 cm^{-1} is most probably due to vibrations of Zr—O bands but this bond is not single but has an increased multiplicity due to the tendency of oxygen to form additional dative bond with Zr to give a situation like $\mathrm{Zr} \overset{\leftarrow}{-} \mathrm{O}$ in oxobridges[10].

The molar conductance values (Table 1) in nitrobenzene are very low which indicates that the compounds behave as nonelectrolytes in solution.

In general, the complexes start losing weight in air above 60° in an exothermic process with the break down of alkoxy groups to olefins (C_3H_6) (actually trapped) forming hydroxo residues accompanied with subsequent or simultaneous elimination of base molecules as such (isolated). This leads to the formation of ZrOCl(OH) at temperatures of ca. 320°. This decomposes to form $\mathrm{ZrO_2}$ at temperatures above 500°. The stepwise schematic decompositions (based on thermal gravimetric differential thermal gravimetric and differential thermal analysis data) are given in Scheme 1.

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