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Note

Complexes of Oxozirconium(IV) Perchlorate, Nitrate and Thiocyanate with Some Heterocyclic Bases

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A number of oxozirconium(IV) perchlorate, nitrate and thiocyanate adducts with various heterocyclic bases have been synthesized. The compounds were characterized by elemental analysis, molar masses, electrical conductance and infrared spectra. In all perchlorate complexes both perchlorate groups are outside the coordination sphere, in nitrate complexes the nitrate groups are bicovalently bonded, while in thiocyanate complexes the thiocyanate groups are *N*-bonded. The coordination number of Zr(IV) in these compounds is either five or seven, depending on the anions present. The thermogravimetric analyses of the compounds are also been given.

INTRODUCTION

A number of papers on the complexes of oxozirconium (IV) with heterocyclic *N*-oxides have been published[1-3]. Comparatively little is known about the complexes of oxozirconium(IV) ion with ligands containing nitrogen as donor atom[4]. In view of this we report here the synthesis and characterization of adducts of the oxozirconium salts with certain heterocyclic nitrogen bases such as pyridine, (py), α-picoline (α-pic), 2:4-lutidine (2,4-LN), 2:6-lutidine (2,6-LN), 2-amino pyridine (NH_2py), quinoline (Q), 2,2'-bipyridine (bipy) and 1,10-phenanthroline(phen).

EXPERIMENTAL

Materials — Zirconyl(IV) nitrate used was obtained from BDH, while perchlorate and thiocyanate were prepared from nitrate as reported earlier[3]. Bases used were obtained commercially.

Preparation of complexes — Perchlorate complexes were synthesized by the method reported earlier[4]. Nitrate and thiocyanate complexes were synthesized by a general procedure. To a solution of metal salt in MeOH (~ 20 ml), an excess of ligand in the same solvent (~ 25 ml) was added. All complexes separated out either immediately or after some time, and were then filtered, washed with MeOH followed by Et_2O and dried in vacuo.

The analyses and physical measurements were performed as reported previously[3].

TABLE I

Analytical Data on the Complexes of Oxozirconium(IV) with N-heterocyclic Bases

Complex	Analysis/% Found (Calcd) Metal	C	H	N	Molar conductivity Λ/Ω^{-1} cm^2 mol^{-1}
$ZrO(ClO_4)_2 \cdot 4$ (Pic)	13.92(13.42)	42.79(42.47)	4.20(4.12)	8.37(8.25)	50.82
$ZrO(ClO_4)_2 \cdot 4$ (NH_2Py)	13.86(13.34)	35.32(35.19)	3.62(3.51)	16.57(16.42)	48.36
$ZrO(ClO_4)_2 \cdot 4$(2, 4LN)	12.10(12.39)	45.90(45.77)	4.96(4.90)	7.89(7.62)	—
$ZrO(ClO_4)_2 \cdot 4$ (2, 6LN)	12.23(12.39)	45.92(45.77)	4.92(4.90)	7.82(7.62)	—
$ZrO(NO_3)_2 \cdot 2$ (Py)	23.09(23.39)	30.39(30.84)	2.64(2.57)	14.51(14.39)	4.9
$ZrO(NO_3)_2 \cdot 2$ (Pic)	22.32(21.82)	34.76(34.53)	3.60(3.35)	13.57(13.42)	—
$ZrO(NO_3)_2 \cdot 2$ (NH_2Py)	21.16(21.71)	28.82(28.63)	2.91(2.86)	20.12(20.04)	5.3
$ZrO(NO_3)_2 \cdot 2$ (2, 4LN)	20.92(20.44)	37.92(37.75)	4.12(4.04)	12.72(12.58)	—
$ZrO(NO_3)_2 \cdot 2$ (2, 6LN)	20.80(20.44)	37.95(37.75)	4.10(4.04)	12.73(12.58)	—
$ZrO(NO_3)_2 \cdot 2$ (Q)	18.21(18.60)	44.32(44.17)	2.91(2.86)	11.67(11.45)	6.9
$Zr(NO_3)_2 \cdot$ Bipy	23.90(23.51)	31.17(31.00)	2.13(2.06)	14.59(14.47)	—
$ZrO(NO_3)_2 \cdot$ Phen	22.32(22.69)	36.10(25.91)	2.16(1.99)	14.12(13.96)	7.3
$ZrO(NCS)_2 \cdot 2$ (Py)	23.16(23.88)	37.52(37.79)	2.81(2.62)	14.74(14.69)	5.1
$ZrO(NCS)_2 \cdot 2$ (Pic)	22.61(22.24)	41.32(41.07)	3.58(3.42)	13.75(13.69)	4.9
$ZrO(NCS)_2 \cdot 2$ (NH_2Py)	22.60(22.14)	35.26(35.03)	3.12(2.91)	20.52(20.43)	5.3
$ZrO(NCS)_2 \cdot 2$ (2, 4LN)	20.16(20.82)	44.10(43.93)	4.20(4.11)	12.97(12.81)	—
$ZrO(NCS)_2 \cdot 2$ (2, 6LN)	20.32(20.82)	44.05(43.93)	4.18(4,11)	12.92(12.81)	—
$ZrO(NCS)_2 \cdot 2$ (Q)	18.32(18.91)	49.93(49.89)	2.83(2.91)	11.81(11.64)	6.9
$ZrO(NCS)_2 \cdot$ Bipy	24.36(24.01)	38.27(37.99)	2.32(2.11)	14.83(14.77)	5.7
$ZrO(NCS)_2 \cdot$ Phen	23.39(23.15)	43.19(42.74)	2.12(2.03)	14.32(14.24)	3.9

TABLE II

IR Absorption Frequencies/(cm^{-1}) of Oxozirconium(IV) Perchlorate Complexes

Complex	C=C, C=N and ring stretching of heterocyclic ring	in -plane ring deformation	out-of-plane ring deformation	ClO_4 ν_4	ClO_4 ν_3	metal-N stretching
$ZrO(ClO_4)_2 \cdot 4$ pic	1625s, 1610m, 1555m, 1485m	640m	420m, 415w	1105sh 1080s	630s 625sh	320m
$ZrO(ClO_4)_2 \cdot 4\,NH_2py$	1680s, 1675sh, 1660s, 1620m, 1550s	642m	425m, 418m	1110s 1095s	630s 625sh	325m
$ZrO(ClO_4)_2 \cdot 4$ (2, 4—LN)	1630s, 1620s, 1490m, 1450m	640m	420m, 415m	1100sh 1090s	635sh 625s	315m
$ZrO(ClO_4)_2 \cdot 4$ (2, 6—LN)	1645s, 1620s, 1575s, 1480s	642m	420m, 415m	1090s 1080sh	630m 620m	312m

TABLE III

IR Absorption Frequencies/(cm^{-1}) of Oxozirconium(IV) Nitrate Complexes

Complex	C=C, C=N and ring stretchings of heterocyclic ring	in-plane ring deformation
$ZrO(NO_3)_2 \cdot 2$ (py)	1640s, 1600s, 1505s, 1490s	638m
$ZrO(NO_3)_2 \cdot 2$ (pic)	1625s, 1610m, 1545m, 1475m	640m
$ZrO(NO_3)_2 \cdot 2$ (NH_2py)	1660m, 1620m, 1560m, 1460s	640m
$ZrO(NO_3)_2 \cdot 2$ (2, 4—LN)	1655m, 1620sh, 1555s, 1450s, br	640m
$ZrO(NO_3)_2 \cdot 2$ (2, 6—LN)	1650s, 1620s, 1580s, 1460s	640m
$ZrO(NO_3)_2 \cdot 2$ (Q)	1635s, 1595s, 1560s	635m
$ZrO(NO_3)_2 \cdot$ bipy	1625s, 1600s, 1590sh, 1450m	662m, 657m, 635m
$ZrO(NO_3)_2 \cdot$ phen	1595s, 1500m, 1470m	665m, 658m, 640m

TABLE IV

IR Absorption Frequencies/(cm^{-1}) of Oxozirconium(IV) Thiocyanate Complexes

Complex	C=C, C=N and ring stretching of heterocyclic ring	in-plane ring deformation
$ZrO(NCS)_2 \cdot 2$ (py)	1625s, 1560m, 1460sh, 1450s	640m
$ZrO(NCS)_2 \cdot 2$ (pic)	1620s, 1610m, 1545m, 1770m	642m
$ZrO(NCS)_2 \cdot 2$ (NH_2py)	1660m, 1600w, 1550m, 1460s	640m
$ZrO(NCS)_2 \cdot 2$ (2, 4—LN)	1620s, br, 1600sh, 1535m	635m
$ZrO(NCS)_2 \cdot 2$ (2, 6—LN)	1640s, 1615m, 1575vs, 1470s	640m
$ZrO(NCS)_2 \cdot 2$ (Q)	1630s, 1590s, 1550s, 1490m	635w
$ZrO(NCS)_2 \cdot$ (bipy)	1620m, 1605m, 1580s, 1565m, 1450s	662m, 655w, 640m
$ZrO(NCS)_2 \cdot$ (phen)	1595s, 1510w, 1495m, 1430m	665m, 660sh, 640m

RESULTS AND DISCUSSION

The analytical data correspond to the compositions $ZrOX_2 \cdot L$ (L = bipy, phen; X = NO_3, NCS), $ZrOX_2 \cdot 2L$ (L = py, pic, NH_2py, 2,4-LN, 2,6-LN, Q; X = NO_3, NCS) and $ZrOX_2 \cdot 4L$ (L = pic, NH_2py, 2,4-LN, 2,6-LN; X = ClO_4). Perchlorato and nitrato complexes are non-hygroscopic while thiocyanato complexes are sensitive to atmospheric moisture. The molar conductances of the complexes in nitrobenzene indicate that nitrato and thiocyanato complexes are non-electrolytes whereas perchlorato complexes are 1 : 2 electrolytes.

The ν(C — C) + ν(C — N) bands, due to substituted pyridines, observed in the 1600—1500 cm^{-1} region in the IR spectra of the complexes, indicate that these ligands are bonded through the nitrogen atom[4-6]. In NH_2py the strong broad band at 3333 cm^{-1}, attributed to (—NH_2) stretching[5], remains unaffected on complexation. The in-plane ring deformation, appearing at ≈ 625 cm^{-1} in the ligands[7] is shifted to a higher wave number and split up into three bands in bipy and phen, while the out-of-plane deformation, observed at ≈ 400 cm^{-1}, is split up into two in py and substituted py[8] and shifts to a higher wave number in bipy and phen on complexation. The presence of ν_3 and ν_4 bands

TABLE III

(Continued)

out-of-plane ring deformation	NO$_3$					($\nu_1 + \nu_4$)	Δ	Zr-O (Nitrate) stretching	Metal ligand stretching
	ν_4	ν_1	ν_2	ν_6	ν_3/ν_5				
422m, 415m	1520m	1290m	1030m	820m	735m	1740w, 1700w	40	235m	305m
420m, 415m	1510m	1290m	1025m	830m	760m	1755m, 1710w	45	240m	310m
425m, 415m	1515m	1300m	1035m	835m	755w	1750w, 1710w	40	235m	320m
425m, 415m	1520m	1310m	1040m	840m	760w	1760w, 1715w	45	235w	315m
420m, 415m	1500m	1280m	1035m	860m	740w	1760w, 1710w	50	240m	320m
425m, 418m	1510m	1300m	1040m	850w	760w	1765w, 1715w	50	240w	355m
415m	1520m	1310m	1035m	840w	740w	1745w, 1705w	40	235m	360m
410m	1520m	1320m	1040m	850w	750w	1750w, 1705w	45	240m	360m

TABLE IV

(Continued)

out-of-plane ring deformation	ν(CN)	ν(CS)	ν(NCS)	ν(Zr-N) thiocyanate	Metal-ligand stretching
425m, 415m	2070s	820m	480m	270m	310m
420m, 415sh	2060s	830m	475m	265w	330m
425m, 415w	2050s	840m	474w	272w	320m
425m, 415sh	2060s	840m	470w	270w	330m
425m, 415w	2070s	830m	475w	265w	325m
425m, 415m	2075s	840m	460w	—	360m
415m	2070s	840m	470m	270w 265sh	355m
412m	2075s	835m	470w	—	365m

in the 1120—1070 and 635—620 cm^{-1} regions respectively, clearly indicate the ionic nature of the perchlorate groups[10,11]. The absence of the ν_3 band of ionic nitrate (D_{3h}) around 1360 cm^{-1} and presence of two strong bands in the region 1530—1500 and 1310—1290 cm^{-1} attributed to ν_4 and ν_1 modes suggest the covalently bonded nitrate groups[12] in these complexes. The two combination bands ($\nu_1 + \nu_4$) appear in 1760—1740 and 1710—1700 cm^{-1} regions and separation[13,14] of these bands varies from 50—35 cm^{-1}, suggest the bidentate nature of nitrato groups in these complexes. The band associated with (Zr—O) (nitrato) in these complexes is tentatively assigned at ca 235 cm^{-1}.[15] In all the thiocyanato complexes the three fundamental frequencies, ν_{C-N} stretch (ν_1), C—S stretch (ν_3) and N—C—S bending (ν_2) fall in the ranges 2080—2050; 865—790 and 480—465 cm^{-1} and clearly indicate the terminal *N*-bonded isothiocyanate to metal ion[16]. The *N*-bonding is further evidenced by ν(Zr — N) absorption (tentatively idenfied) at ca 270 cm^{-1}.[17] The metal-ligand vibrations in these complexes have been tentatively assigned in 360—300 cm^{-1} region[4]. The Zr = O characteristic band is observed in the complexes as a weak band in the 980—900 cm^{-1} region.[1-3]

The weight loss values observed in the thermal decomposition of some of the oxozirconium(IV) complexes correspond very closely with the following schemes:

(1) $ZrO(ClO_4)_2 \cdot 4L \xrightarrow{t_1} ZrO\,(ClO_4)_2 \cdot 2L \xrightarrow{t_2} ZrO(ClO_4)_2 \cdot \xrightarrow{t_3} ZrO_2$.
L = pic; $t_1 = 230\,^{\circ}C$; $t_2 = 410\,^{\circ}C$; $t_3 = 525\,^{\circ}C$; $L = NH_2py$; $t_1 = 240\,^{\circ}C$; $t_2 = 480\,^{\circ}C$; $t_3 = 530\,^{\circ}C$; L = 2,4—LN; $t_1 = 225\,^{\circ}C$; $t_2 = 425\,^{\circ}C$; $t_3 = 530\,^{\circ}C$.

(2) $ZrO(NO_3)_2 \cdot 2L \xrightarrow{t_1} ZrO(NO_3)_2 \xrightarrow{t_2} ZrO_2$
L = py; $t_1 = 270\,^{\circ}C$; $t_2 = 485\,^{\circ}C$; $L = NH_2py$; $t_1 = 310\,^{\circ}C$; $t_2 = 505\,^{\circ}C$; L = Q; $t_1 = 290\,^{\circ}C$; $t_2 = 490\,^{\circ}C$.

(3) $ZrO(NCS)_2 \cdot 2L \xrightarrow{t_1} ZrO(NCS)_2 \xrightarrow{t_2} ZrO_2$
L = pic; $t_1 = 280\,^{\circ}C$; $t_2 = 470\,^{\circ}C$; $L = NH_2py$; $t_1 = 295\,^{\circ}C$; $t_2 = 490\,^{\circ}C$; L = 2,4—LN; $t_1 = 245\,^{\circ}C$; $t_2 = 485\,^{\circ}C$.

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SAŽETAK

Kompleksi oksocirkonij(IV)-perklorata, -nitrata i -tiocijanata s nekima heterocikličkim bazama

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Pripravljen je niz spojeva oksocirkonij(IV)-perklorata, -nitrata i -tiocijanata s različitima heterocikličkim bazama. Ti su spojevi karakterizirani elementnom analizom, termogravimetrijski, određivanjem moralne mase i električke vodljivosti te infracrvenim spektrima. U svima perkloratnim kompleksima obje perkloratne skupine nalaze se izvan koordinacijske sfere, u nitratnim su kompleksima nitratne skupine vezane bikovalentno, a tiocijanatne su skupine vezane preko dušikova atoma. Ovisno o anionu, koordinacijski broj cirkonija(IV) iznosi 5 ili 7.