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Original Scientific Paper

## Infrared Studies of Some Selenocyanato Complexes of Oxozirconium(IV) with O and N Donor Ligands

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A series of new complexes of oxozirconium(IV) selenocyanate with different ligands has been prepared. The IR spectra (4000—200  $\text{cm}^{-1}$ ) of free ligands and complexes indicate coordination through either oxygen or nitrogen, depending on the type of the ligand.

Structural investigations of several oxozirconium (IV) thiocyanate complexes have been reported in previous papers<sup>1-5</sup>. Selenocyanate group offers interesting bonding possibilities<sup>6</sup>. In metal ion complexes it may coordinate through either nitrogen ( $\text{M}-\text{NCSe}$ )<sup>7</sup>, selenium ( $\text{M}-\text{SeCN}$ )<sup>8</sup> or bridging ( $\text{M}-\text{SeCN}-\text{M}$ )<sup>9</sup>. Examples of complexes containing all types of selenocyanate bonding are also known. No attempt has been made so far to investigate the complexes of oxozirconium (IV) selenocyanate. It was, therefore, considered worthwhile to study the complexes formed by oxozirconium (IV) selenocyanate with antipyrine (apy); 4-amino antipyrine (aapy), pyridine *N*-oxide (pyo); 2,2'-bipyridyl *N-N'*-dioxide (bipyo<sub>2</sub>); triphenyl phosphine oxide (tppo); bis (tri *n*-butyl tin) oxide (tbto); pyridine (py); 2,4-lutidine (ln); 2,2'-bipyridyl (bipy); 1,10-phenanthroline (phen); hydrazine (hy) and phenyl hydrazine phhy).

Stoichiometries of the isolated complexes have been established by elemental analyses (Table 1). All the complexes are non-hygroscopic and quite stable. The molar conductances of  $10^{-3}$  M solution in acetonitrile are within the range 4.9—6.3  $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$  indicating the absence of ionic species.

The infrared spectra of the free ligands and the complexes were recorded in the 4000—200  $\text{cm}^{-1}$  region. The positions of the  $\text{X}=\text{O}$  ( $\text{X}=\text{C}, \text{N}$  or  $\text{P}$ ) stretching bands in all oxygen donor ligands are significantly different in the complexes (Table II). A marked negative shift in  $\nu(\text{X}=\text{O})$  from free ligands in all the complexes confirm the oxygen linkage between the metal and ligands<sup>10,11</sup>. The IR studies also reveal bidentate nature of aapy and bipyo<sub>2</sub> coordination occurring through amino nitrogen and carbonyl oxygen in case of aapy and through both the oxygen atoms of bipyo<sub>2</sub><sup>10,11</sup>. The  $\text{Sn}-\text{O}-\text{Sn}$  stretching absorption which occurs at 783  $\text{cm}^{-1}$  in free tbto<sup>12</sup>, shifts on

TABLE I  
Analytical Data of Oxozirconium(IV) Complexes

Complex	% Analysis Found (Calcd)			
	Zr	C	H	N
ZrO(SeCN) <sub>2</sub> · 2apy	13.49(13.13)	41.78(41.55)	3.57(3.46)	12.32(12.12)
ZrO(SeCN) <sub>2</sub> · aapy	17.72(17.50)	30.12(30.00)	2.61(2.50)	13.59(13.46)
ZrO(SeCN) <sub>2</sub> · 2pyo	17.69(17.94)	28.59(28.40)	2.01(1.97)	11.32(11.04)
ZrO(SeCN) <sub>2</sub> · bipyo <sub>2</sub>	18.32(18.01)	28.73(28.51)	1.69(1.58)	11.34(11.08)
ZrO(SeCN) <sub>2</sub> · 2tppo	10.61(10.42)	52.69(52.23)	3.72(3.43)	3.42( 3.20)
ZrO(SeCN) <sub>2</sub> · 2tbto	6.21( 6.03)	39.98(39.76)	7.42(7.15)	1.92( 1.85)
ZrO(SeCN) <sub>2</sub> · 2py	19.31(19.15)	30.72(30.31)	2.31(2.10)	11.98(11.78)
ZrO(SeCN) <sub>2</sub> · 2bn	17.36(17.13)	36.70(36.15)	3.51(3.38)	10.69(10.54)
ZrO(SeCN) <sub>2</sub> · bipy	19.49(19.23)	30.82(30.44)	1.78(1.69)	11.57(11.83)
ZrO(SeCN) <sub>2</sub> · phen	18.56(18.30)	33.60(33.80)	1.68(1.60)	11.49(11.26)
ZrO(SeCN) <sub>2</sub> · 2hy	23.97(23.88)	6.41( 6.29)	2.30(2.09)	22.19(22.04)
ZrO(SeCN) <sub>2</sub> · 2pphy	17.32(17.07)	31.79(31.51)	3.12(3.00)	15.92(15.75)

coordination to 710 cm<sup>-1</sup> indicates the metal-oxygen linkage in the complex<sup>13</sup>. The metal-oxygen stretching vibrations occur in all these complexes in the region 390—360 cm<sup>-1</sup><sup>1-3,13</sup>.

In complexes with heterocyclic ligands, several strong absorptions in the spectra of free bases occur in the 1625—1400 cm<sup>-1</sup> region and have been attributed to C=C, C=N and ring stretchings. Out of these, the absorptions associated with the cyclic ring are apparently unaffected on complexation, while those arising from the heterocyclic ring are shifted to higher frequencies due to tightening of the ring on coordination with hetero N-atom<sup>14,15</sup>. In the IR spectra of hydrazine and phenyl hydrazine complexes the two bands in the 3000 cm<sup>-1</sup> region and one band at the 1600 cm<sup>-1</sup> region observed, which are obviously the result of N—H stretching and bending vibrations respectively and are lower in frequency than the bands observed in gaseous hydrazine<sup>16</sup> and phenyl hydrazine<sup>17</sup>, clearly indicates that these ligands are coordinated through nitrogen atom. The bidentate behaviour of these ligands is further confirmed by the presence of N—N stretching frequency<sup>18</sup> around 955 cm<sup>-1</sup>. M—N stretching frequency in all these complexes<sup>14,15,17</sup> fall within the region 385—360 cm<sup>-1</sup>.

The intensity of the CN stretching band is useful in distinguishing the N- and Se-bonded complexes<sup>7</sup>. The  $\nu$ (CN),  $\nu$ (CSe) and  $\delta$ (NCSe) in all the complexes occur at 2080—2050; 695—625 and 435—420 cm<sup>-1</sup> region respectively thus indicating the N-bonded selenocyanate group<sup>7-9</sup>. N-bonding is further evidenced by the presence of bands in region 250—215 cm<sup>-1</sup> due to  $\nu$ (Zr—N) (selenocyanate). A medium intensity band in the 960—900 cm<sup>-1</sup> region is assigned as (Zr=O) stretching mode in all the complexes<sup>1,2,19</sup>.

TABLE II  
 Infrared Data of Oxozirconium(IV) Complexes

Complex	Selenocyanate vibrations				$\nu$ (X = O) (X = C, N or P)		$\nu$ (M = X) X = O or N
	$\nu$ (CN)	$\nu$ (C—Se)	$\delta$ (NCSe)	$\nu$ (Zr—N)	Ligand	Complex	
ZrO(NCSe) <sub>2</sub> · 2apy	2065 s	690 m	430 m	220 m	1660 s	1575 s 1565 s	380 m
ZrO(NCSe) <sub>2</sub> · aapy	2070 s	695 m	425 m	215 m	1670 s 1640 s	1560 vs	385 m 350 m
ZrO(NCSe) <sub>2</sub> · 2pyo	2075 s	690 m	430 m	225 m	1265 s	1220 s	380 m
ZrO(NCSe) <sub>2</sub> · bipyo <sub>2</sub>	2070 s	685 m	430 m	230 m	1264 s 1260 s	1255 s 1220 s	390 m
ZrO(NCSe) <sub>2</sub> · 2tppo	2070 s	695 m	420 w	—	1195 s	1120 s	380 m
ZrO(NCSe) <sub>2</sub> · 2tbto	2080 s	675 w 625 m	—	220 m	$\nu$ (Sn—O—Sn) 783 s 710 s		390 mpr
ZrO(NCSe) <sub>2</sub> · 2py	2070 s	685 m	420 m	250 m, br		C=C, C=N and ring stretching of heterocyclic ring 1625 mbr, 1600 m, 1530 mbr, 1490 m	380 m
ZrO(NCSe) <sub>2</sub> · 2bn	2080 s	650 m	430 m	—	1620 vs br, 1560 sh, 1525 m		365 m
ZrO(NCSe) <sub>2</sub> · bipy	2050 m	685 m	430 m	232 m	1620 m, 1595 s, 1525 vs, 1495 m, 1470 m		360 m
ZrO(NCSe) <sub>2</sub> · phen	2080 m	650 m	420 m	250 m, br	1625 m, 1516 m, 1585 m, 1540 sh, 1520 s, 1490 sh, 1415 m	$\nu$ (NH) $\delta$ (NH) $\nu$ (N—N)	370 m
ZrO(NCSe) <sub>2</sub> · 2hy	2065 m	690 m	435 m	235 w	3230 m, 1600 br, 955 m 3190 m		385 m
ZrO(NCSe) <sub>2</sub> · 2phhy	2060 m	690 m	—	225 w	3220 s, 1610 m, 980 w, 1595 s		375 m

## EXPERIMENTAL

Oxozirconium(IV) selenocyanate was prepared in solution by mixing methanolic solutions of  $ZrO(NO_3)_2$  and  $KNCSe$  in 1:2 ratio and filtering out the precipitated  $KNO_3$ . Since  $ZrO(SeCN)_2$  solution has a tendency to decompose to a red coloured solution, it should be used immediately after filtration.

The complexes were prepared by mixing methanolic solutions of  $ZrO(SeCN)_2$  and the ligand in required molar proportion and the reaction mixture was shaken thoroughly. Some complexes separated out either immediately or after a certain period of time. All the complexes were suction filtered, washed with methanol followed by ether and dried in vacuo over  $P_4O_{10}$ .

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## SAŽETAK

**IR studij oksocirkonij(IV) selenocijanato kompleksa s O i N donorskim ligandima**

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Pripravljen je niz novih kompleksa oksocirkonij(IV) selenocijanata s različitim ligandima. Infracrveni spektri, snimljeni u području od 4000 do 200  $cm^{-1}$ , ukazuju na koordinaciju preko kisika ili dušika, ovisno o tipu liganda.