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Spectroscopic Characterization of Oxozirconium(IV) Isothiocyanates

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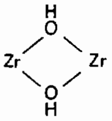
Abstract

The infrared (4000–400 cm^{-1}) and Raman (2000–50 cm^{-1}) spectra of solid oxo–zirconium(IV) isothiocyanates formulated as $[ZrO(NCS)_3]M \cdot 2H_2O$ with M = Cs^+ or pyH^+ were investigated. An assignment of the vibrational spectra is given. Two bands at 916 cm^{-1} and 615 cm^{-1} are interpreted as being due to different bridged oxo–zirconium modes in an oligomeric structure.

Introduction

Structural studies reported to date have shown that oxo-zirconium salts form a class of compounds with a complex nature. They appear to be oligomers or polymers with double oxide or hydroxide bridges as the bonding units [1],



The predominant coordination number of Zr(IV) in these salts is eight, and the ZrO_8 polyhedra units have either the symmetry of a dodecahedron or an antiprism. No X-ray evidence has been found for the presence of the zirconyl cation, ZrO^{+2}, which has been frequently formulated as the structural unit of oxo-zirconium salts on the basis of an IR band at approximately 900 cm^{-1}, in the range of metal–oxygen double bonds [2]. We report here the complete infrared and Raman spectra of $[ZrO(NCS)_3]M \cdot 2H_2O$, with M = Cs^+ or PyH^+ as solid powders. An assignment is also proposed which is in good agreement with the known structures for the oxo-zirconium salts.

Experimental

The complexes were prepared as white solid powders, following previously described procedures [3]. Infrared spectra (4000–350 cm^{-1}) were recorded in a Perkin Elmer 225 spectrometer. The samples were in the form of KBr disks or nujol mulls. The wavelengths of the IR absorptions were taken as the approximate center in the broad bands. Raman spectra (2000–50 cm^{-1}) were recorded on the solid powder with a Jarrel Ash 125 equipped with an argon laser for the 488.0 and 514.5 nm excitations.

Results and Discussion

IR and Raman spectra of $[ZrO(NCS)_3]M \cdot 2H_2O$ are shown in Figs. 1–4 and the wavelengths are listed in Table I. A comparative analysis shows that three groups of common vibrations can be seen in these spectra: 1) the very broad band in the range 3600–2800 cm^{-1} and the band at 1600 cm^{-1}; 2) bands in the ranges 2100–2000 cm^{-1},

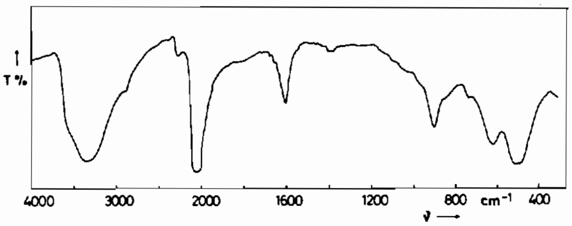


Fig. 1. Infrared spectrum of $[ZrO(NCS)_3]Cs \cdot 2H_2O$.

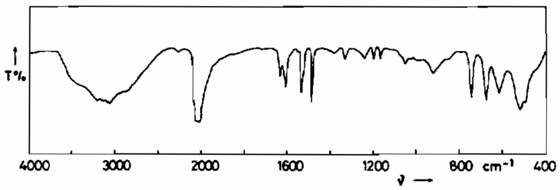


Fig. 2. Infrared spectrum of $[ZrO(NCS)_3]PyH \cdot 2H_2O$.

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TABLE I. Main Vibrational Frequencies of solid $[ZrO(NCS)_3]M \cdot 2H_2O$ ($M = Cs^+$ or PyH^+).

$ZrO(NCS)_3M \cdot 2H_2O$		$ZrO(NCS)_3M \cdot 2H_2O$		Assignment
Raman (cm^{-1})	IR (cm^{-1})	Raman (cm^{-1})	IR (cm^{-1})	
87				
136				Skeletal vibr.
196s		195s		
		255m		
292m				Zr–NCS stretching
432m		435m	450sh	
	485s	490m	490s	NCS o.p. deform.
510m	508s	515m	515s	
	615m	620vw	615m	Zr–O bridge vibr.
			675s	
			745s	
835m	825w	850m	845w	C–S stretching
914vw	914m		918m	Zr–O bridge vibr.
		1010s	1030w	
		1042s	1050w	
			1165w	
			1198w	PyH^+ vibrations
			1240w	
			1295w	
			1488m	
			1535m	
	1610m		1610m	H_2O deformation
			1627m	
		2045m		
2060				C≡N stretching
2088vs	2100–2000vs,br		2100–2000vs,br	
2110	3600–2700vs,br		3600–2500vs,br	O–H stretching

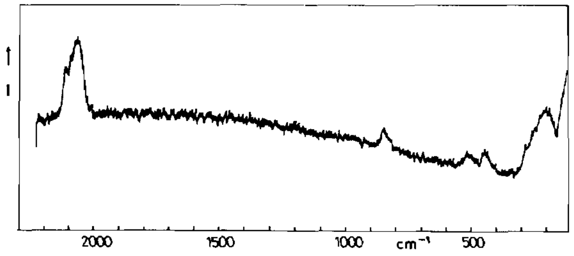

Fig. 3. Raman spectrum of $[ZrO(NCS)_3]Cs \cdot 2H_2O$.

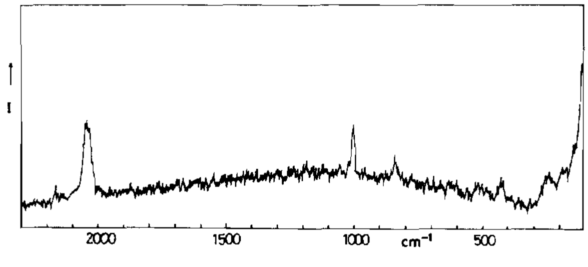

Fig. 4. Raman spectrum of $[ZrO(NCS)_3]PyH \cdot 2H_2O$.

835 cm^{-1} and 510–480 cm^{-1}, and 3), bands at 916 cm^{-1} and at 615 cm^{-1}. The remaining absorptions shown in Figs. 2 and 4 and not included in the above groups are due to the PyH^+ cation vibrations.

Group 1 is due to the water-normal modes, the ν(OH) antisymmetric and symmetric stretching modes at 3600–2800 cm^{-1} and the β(H–O–H) deformation modes at *ca.* 1600 cm^{-1}. The presence of such a broad ν(OH) band is usually taken as being indicative of a hydrogen bonding in the solid compound.

Group 2 vibrations are the normal three modes expected for the thiocyanate ligand, NCS: ν(CN), ν(CS) and δ(NCS). This linear and ambidentate ligand can bind to transition metals via either its nitrogen atom, M–NCS(isothiocyanates) or its sulfur atom, M–SCN(thiocyanates). Other structures involving NCS bridges are possible but the overall simplicity of the spectra does not justify consideration. The metal–isothiocyanate and metal–thiocyanate complexes have been the subject of many IR spectral investigations, mostly from the point of view of differentiating the M–NCS and M–SCN bondings by the frequency ranges of the ν(CN) and ν(CS) stretching vibrations [4]. The ν(CN) range values generally appear to increase from M–NCS (2100 cm^{-1} or below) to M–SCN (2130–2100 cm^{-1}), whereas the ν(CS) range is higher for M–NCS (860–780 cm^{-1}) than for M–SCN (720–690 cm^{-1}).

A third criterion for the correlation of spectral ranges with N and S metal bonding are the deformation δ(NCS) modes, being in the range 490–440 cm^{-1} for isothiocyanates and 440–410 cm^{-1} for thiocyanates.

The IR ν(CS) mode, although rather broad and weak, has proved to be a good structural diagnostic of the type of bonding, much more reliable than the ν(CN) mode. This band cannot always be unequivocally identified, especially in the presence of other organic ligands or counterions when they absorb in this range or may sometimes be confused with the first δ(NCS) overtones. This uncertainty can be removed when Raman data are available, since the Raman counterpart should be a well-defined and intense line of the highly polarizable C–S bond. Spectroscopic studies of transition metal thiocyanates rarely include Raman data, due to the relatively high absorptions by these coloured compounds of the exciting Raman line, thus yielding unsatisfactory Raman spectra.

We succeeded in recording the, complete Raman spectra of the white solid complexes $[ZrO(NCS)_3]$-$M\cdot 2H_2O$ in the range of interest. The strong I.R. and Raman bands around 2050 cm^{-1} are consistent with a Zr–NCS bonding, though this does not constitute unequivocal proof. The IR spectrum shows two bands and the Raman shows at least three distinct lines overlapping in this range (not shown in the Figs. 1 to 4), most probably due to site symmetry and correlation effects. The weak ν(CS) mode at *ca.* 835 cm^{-1} has its Raman counterpart of medium intensity and thus can be unambiguously assigned to the CS stretching mode of the Zr–NCS bonding, indicating that the NCS group is N-bounded to Zr. No other lines which could be ascribed to any different C–S bonds, such as in free thiocyanate, as would be the case in a double salt $ZrO(NCS)_2\cdot$ $NCSM\cdot nH_2O$, in S–metal bonding M–SCN or in bridging bondings (Figs. 3, 4 and 5) were observed.

The IR and Raman vibrations at 508 and 485 cm^{-1} of medium intensity are characteristic of the degenerate δ(NCS) vibrations when NCS coordinates through N to the metal. The shoulder at 440 cm^{-1} can be assigned to the activated A_1 mode of the NCS which has its Raman counterpart at 440 cm^{-1}. The weak Raman line at 292 cm^{-1} may be ascribed to the metal–ligand mode ν(M–NCS), in accordance with the assignment given for $Zr(NCS)_6(Et_4N)_2$ [5]. The small atomic weight of N and the low values for ν(M–NCS) indicate that the frequency of this vibration is determined to a large extent by the whole thiocyanate group. Raman lines below 200 cm^{-1} may be ascribed to the various deformation modes of the metal–ligand skeleton.

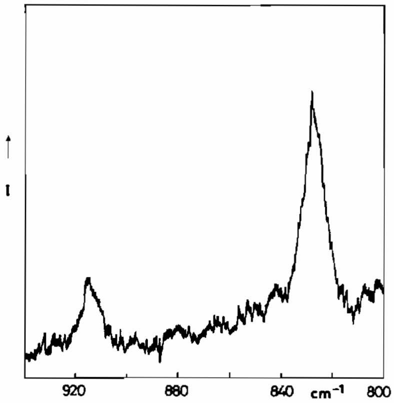

Fig. 5. Raman spectrum of $[ZrO(NCS)_3]Cs\cdot 2H_2O$ in the 940–800 cm^{-1} range.

In the third group of common vibrations mentioned above we include the bands at 916 and at 615 cm^{-1} of medium intensity in the IR spectrum and very weak in the Raman, and assign them to different zirconium–oxygen modes. Previous IR assignments based on the sole existence of a ZrO^{+2} unit could not account for the bands at 615 cm^{-1} [3]. The criteria used in the present assignment were the following:

(a) infrared spectra of the complexes $Zr(NCS)_6$-$(Et_4N)_2$ and $Zr(NCS)_2(Cp)_2$ show, in addition to the bands due to Et_4N^+ and Cp^-, the characteristic thiocyanate bands at 1985, 870 and 499 cm^{-1} and at 2003 and 497 cm^{-1} [5]. The ν(CS) band in the second complex is overlapped by the Cp^- vibrations. These Zr(IV) isothiocyanate spectra show that the absorption bands around 900 and 600 cm^{-1} are absent from the spectra of compounds where no Zr–O bonding is present. We therefore assign these two bands at 916 cm^{-1} and at 615 cm^{-1} to zirconium–oxygen vibrations.

(b) the M=O double bonds for M: V, Cr, Re, Mo and W are known to give IR absorption bands in the 1050–830 cm^{-1} region. Although no such discrete Zr=O bonds were actually found in basic zirconium salts, the band at 916 cm^{-1} may be described, by analogy, to a zirconium–oxygen double bond character vibration.

(c) X-ray structural data for monoclinic ZrO_2 show that each Zr atom is surrounded by seven oxygens distributed along an irregular polyhedra with very low symmetry [6]. The Raman spectrum shows numerous lines in the 700–50 cm^{-1} range, Fig. 6. The lines in the 700–600 cm^{-1} range should correspond to the highest stretching vibration values of single zirconium–oxygen bonds. We assign then, the vibrational modes at 615 cm^{-1} to oxo–zirconium bonds of near first order.

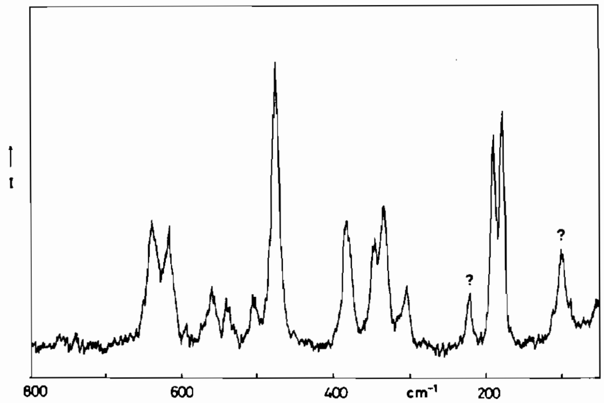

Fig. 6. Raman spectrum of solid powder ZrO_2.

Arguments (a) to (c) strongly suggest that the bands at 916 and 615 cm^{-1} correspond to zirconium–oxygen modes of different bond orders. The band at 916 cm^{-1} may be described as a near-double bond and the band at 615 cm^{-1} as a near-single bond vibration.

It is noteworthy that the X-ray spectra of zirconyl chloride, $ZrOCl_2 \cdot 8H_2O$, shows that the structural unit is a tetramer which has been formulated as $[Zr_4(OH)_8(H_2O)_{16}]^{+8}$, with four double oxide bridges [7]. Even in HCl solutions 0.5 to 2.5 M, X-ray dispersion studies indicate the existence of tetrameric and trimeric ions [8]. As was mentioned above, the double oxide of hydroxide bridges constitute the bonding units in all oxo-zirconium salts studied to date. These include in addition to the water soluble oligomers, $ZrOX_2 \cdot 8H_2O$ (X = Cl or Br) various polymeric sulfates, chromates and nitrates. If we assume the isothiocyanates also contain this basic unit in an oligomeric structure, the bands at 916 cm^{-1} and at 615 cm^{-1} could alternatively be attributed to the vibrations of the antisymmetric and symmetric stretching modes of the zirconium–oxygen bridge bonds. A similar assignment was recently proposed for the binuclear W(V) mono- and di-oxo bridge complexes with 1,1 dithiolate ligands [9].

Shifts resulting from deuteration are in agreement with the latter assignment: $\nu(OH)$ and $\beta(H_2O)$ shifts are the normal expected for these modes, but the bands at 916 and 615 cm^{-1} are rather insensitive to substitution with shifts of no more than 1%. These results suggest that the zirconium–oxygen framework is very rigid, that the OH bonds are of ionic character, and that the oxygens are the main atoms involved in the displacements of these vibrations.

With the results here reported, X-ray structural studies of these interesting compounds appear justified, with expectations for high coordination around the metal atom, probably of oligomeric form with oxide or hydroxide bridges, and perhaps two different functionalities for the oxygen atoms involved in the coordination.

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