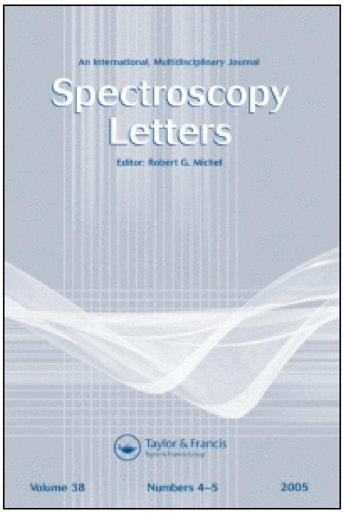

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Infrared Spectrum of the Oxovanadium Complex of Isotopically Labelled *N*-Salicylideneglycinate

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INFRARED SPECTRUM OF THE OXOVANADIUM COMPLEX OF ISOTOPICALLY LABELLED *N*-SALICYLIDENEGLYCINATE

KEY WORDS: *N*-Salicylideneglycinate complex, infrared spectrum, isotopically labelled IR spectra

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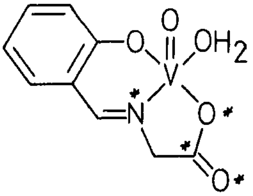
ABSTRACT

The IR spectra of ^{15}N-, ^{18}O- and ^{13}C-labelled [VO(sal-gly)(H_2O)] (sal-gly = *N*-salicylideneglycinate) derived from labelled glycine, and the unlabelled analogue are discussed. Assignments of the characteristic ligand and metal-ligand vibrations are based on the effects of the isotopic substitutions.

INTRODUCTION

The limited extent to which the IR spectra of Schiff base complexes have been studied is probably due to the structural variation of the complexes, the difficulty of applying normal coordinate treatments to the assignment problem and the complexity of the spectra which results from the different metal-ligand bands and extensive vibrational coupling. In previous papers [1-3] we have discussed the IR spectra of *N*-arylsalicylald imine and *N*-salicylideneglycinate complexes by observing the effects of ^{15}N-labelling and metal ion substitution on the spectra. Recent investigations[4-5] on the IR pleochroism of single crystals of metal(II) *N*-methylsalicylaldimines indicate that the lower frequency region contains many skeletal deformation modes and that no pure metal-ligand vibrations are present. In Formula (I), which illustrates the structure of the complex , the atoms which were isotopically substituted are marked with asterisks. It has been established that this complex is five-coordinate, probably with a distorted square base pyrimidal structure.



(I)

EXPERIMENTAL

[VO(sal-gly)(H_2O)] was prepared by the method previously described [6]. The ^{15}N-, ^{18}O-, and ^{13}C-labelled complexes were prepared from ^{15}N-glycine of 95 atom-% purity, ^{18}O-glycine of 78 atom-% purity and 1-^{13}C-glycine of 93 atom-% purity supplied by Prochem Ltd. Analytical data are given in Table 1. IR spectra were determined on Nujol or hexachlorobutadiene mulls between caesium iodide plates (or below 250 cm^{-1}, between polyethylene plates) on a Perkin-Elmer 180 Spectrophotometer.

TABLE 1

Analytical data on [VO(sal-gly)(H_2O)]

N isotope	O isotope	C isotope	Calc./Found %C	%H	%N
^{14}N	^{16}O	^{12}C	41.2	3.5	5.3
			41.1	3.4	5.3
^{15}N	^{16}O	^{12}C	41.1	3.5	5.7
			40.9	3.5	5.8
^{14}N	^{18}O	^{12}C	40.8	3.4	5.3
			40.7	3.5	5.2
^{14}N	^{16}O	^{13}C	41.5	3.5	5.3
			41.0	3.5	5.3

RESULTS AND DISCUSSION

Table 2 lists the assigned bands in the spectrum of [VO(sal-gly)(H_2O)] together with the shifts induced by ^{15}N-, ^{18}O- and ^{13}C-labelling. νC=N, νC=O, νC-N and the CO_2 scissoring and rocking modes have been assigned by virtue[7] of their large isotopic shifts. These assignments are substantiated by earlier reports of labelling studies[3,7] and empirical considerations[8] of the spectra of related complexes and ligands. In the spectra of the unlabelled and ^{15}N-labelled complexes, the carbonyl stretching frequency masks the phenyl vibration, however, this vibration is clearly visible at 1600 cm^{-1} in the spectra of the ^{18}O- and ^{13}C-analogues. νC-O(aryl) is assigned, by its insensitivity to isotopic substitution, to

Table 2

Frequencies (cm^{-1}), ^{15}N-induced shifts ($\Delta\nu^{15}N$), ^{18}O-induced shifts ($\Delta\nu^{18}O$), ^{13}C-induced shifts ($\Delta\nu^{13}C$) and assignments in the IR spectrum of [VO(sal-gly)(H_2O)] (formula I) (all other bands above 600 cm^{-1} shift <1.5 cm^{-1} and below 600 cm^{-1} shift <1 cm^{-1}).

ν^a	$\Delta\nu^{15}N$	$\Delta\nu^{18}O$	$\Delta\nu^{13}C$	Assignments
1636	-12	+1		νC=N
1594		-21	-33	νC=O
1547	-2			
1449	-5			δC-H + νC=N
1416	-3	-3.5	-4.5	δC-H + νC-CO [b]
1395	-3			δC-H + νC-N
1371	-4	-14	-23	νC-O(alkyl)[b]
1331				νC-O(aryl)
1295		-3	-3	impure vibration[b]
1072	-19			νC-N
1005				νV=O
1002(sh)	-2		-3	impure vibration[b]
962		-17	-4	CO_2 scissor
944		-13	-4	
747		-20	-5	CO_2 rock
663(br)				H_2O wag
578	-2	-4	-1.5	ring deformation
567		-4	-8	CO_2 wag
544				νV-O(aryl)
536	-3.5	-5.5	-2.5	νV-N + δCO_2
515		-2	-1.5	coupled δCO_2
483	-2.5	-2.5		νV-N + νV-O(alkyl)
408		-6		νV-O(alkyl)
379		-5.5	-1.5	νV-O(alkyl) + δCO_2
357	-2			δO=V-N
338		-2		δO=V-O(alkyl)
332(sh)		-2.5		
285	-1.5	-2		δN-V-O(alkyl)
277(sh)	-2	-2		
245		-2		δO-V-O(alkyl)
216		-2		

[a] sh = shoulder ; br = broad : [b] see text

the band at 1331 cm^{-1} where it has been similarly assigned in metal(II) salicylaldimines[1-2] and salicylaldehydes[9]. Furthermore a band near here has been assigned as skeletal stretching in *N*-methylsalicylaldimine complexes[4-5]. The sharp and intense band at 1005 cm^{-1} is undoubtedly[6,10-11] the vanadyl stretching frequency, $\nu V{=}O$. The H_2O wagging vibration is reliably assigned[12] to the broad band at 663 cm^{-1}. This assignment is supported by the lack of sensitivity of this band to isotopic labelling.

It has been established[7] that a comparison of the observed isotopic shift with that calculated for the corresponding diatomic oscillator provides a good indication of the vibrational purity of the stretching vibration if most of the energy of vibration is centred in the diatomic group. Favourable comparisons have also been obtained[7] for bending vibrations. Thus the shift observed for $\nu C{=}N$ indicates[7] it is an impure vibration while those observed for $\nu C{=}O$ suggest[7] it has a reasonable degree of purity.

Two bands in the 1450 - 1370 cm^{-1} region are sensitive to ^{15}N-labelling while a further two are sensitive to all three forms of isotopic substitution. Since many bands in this region have been reported to be skeletal and C-H deformations in metal(II) *N*-methylsalicylaldimines[4-5], and because of the small shifts observed, the band at 1449 cm^{-1} is assigned as $\delta C{-}H + \nu C{=}N$ while that at 1395 cm^{-1} is assigned as $\delta C{-}H + \nu C{-}N$. The 1416 cm^{-1} band is probably $\delta C{-}H + \nu C{-}CO_2$ coupled to some nitrogen mode. $\nu C{-}CO_2$ has been reported near here for amino acids[7]. $\nu C{-}O$(alkyl) is assigned by its relatively large ^{18}O- and ^{13}C-shifts to the band at 1371 cm^{-1}. The ^{15}N-sensitivity possibly results from coupling to the other ^{15}N-sensitive bands in this region or to a CCN out-of-phase stretch reported[7] in this region for amino acids.

The weaker ^{18}O- and ^{13}C-shifts of the band at 1295 cm^{-1} shows it to be an impure vibration. Possible assignments are coupled C=O bending + C-C stretching (observed here in the spectra of labelled ketones[7]), coupled δC-C=O or coupled ν$C-CO_2$[7]. The shoulder at 1002 cm^{-1} ($\Delta\nu^{15}N$ □ -2 cm^{-1}) is probably an impure δC-C=N which is coupled to a C-C vibration ($\Delta\nu^{13}C$ = -3 cm^{-1}). More definite assignments in this region above 600 cm^{-1} could only be made after further labelling studies with ^{13}C and, perhaps, deuterium substitution.

Table 2 reveals that many of the bands below 600 cm^{-1}, where the metal-ligand vibrations and ring deformation modes are expected to occur, are sensitive to isotopic labelling, with 60% of the ^{18}O-sensitive bands observed in the spectrum of this complex being found in this region. Because of the small isotopic shifts, it is evident that the majority of the bands in this region are impure vibrations. The band at 578 cm^{-1} is assigned as a ring deformation, being sensitive to all forms of isotopic replacement. The CO_2 wagging vibration expected below 600 cm^{-1} is undoubtedly the band at 567 cm^{-1}. νV-O(aryl) is assigned to the 544 cm^{-1} band which is unaffected by the heavier isotopes. νM-O has been reported in this position in metal salicylaldehydes[9].

The band at 536 cm^{-1}, which is moved to lower frequency by each isotope, is assigned as νV-N + δCO_2. This band is unlikely to be a ring deformation mode because it is the one most shifted by ^{15}N. We therefore prefer to suggest it has νV-N character. The other band having νV-N character occurs at 483 cm^{-1} and appears coupled to νV-O(alkyl). The least-coupled νV-O(alkyl) band is at 408 cm^{-1} ($\Delta\nu^{18}O$ □ -6 cm^{-1}). This relatively large shift suggests it is a fairly pure vibration. The neighbouring band at 379 cm^{-1} which shows a smaller ^{18}O-shift as well as being ^{13}C-sensitive is assigned as νV-O(alkyl) + δCO_2. The 357 cm^{-1} band is assigned as δO=V-N rather than νV-N because the ^{15}N-shift is smaller than observed for the bands at 483 and 536 cm^{-1}. Support for our proposal that the remaining bands between 340 and 200 cm^{-1} are various vanadium-ligand bending modes is provided both by their position and by their small isotopic shifts.

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