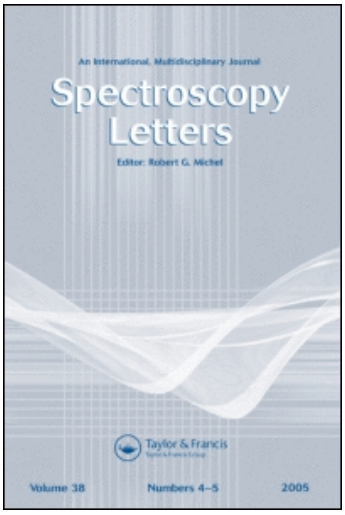

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Band Assignments in the Infrared Spectrum of Zinc Acetylacetonate Monohydrate by ^{18}O-, ^{68}Zn-, and ^{64}Zn-Labelling

Margaret L. Niven[a]; David A. Thornton[a]
[a] Department of Inorganic Chemistry, University of Cape Town, Rondebosch, South Africa

To cite this Article Niven, Margaret L. and Thornton, David A.(1980) 'Band Assignments in the Infrared Spectrum of Zinc Acetylacetonate Monohydrate by ^{18}O-, ^{68}Zn-, and ^{64}Zn-Labelling', Spectroscopy Letters, 13: 6, 419 — 425
To link to this Article: DOI: 10.1080/00387018008064033
URL: http://dx.doi.org/10.1080/00387018008064033

SPECTROSCOPY LETTERS, 13(6), 419-425 (1980)

BAND ASSIGNMENTS IN THE INFRARED SPECTRUM OF ZINC ACETYLACETONATE MONOHYDRATE BY ^{18}O-, ^{68}Zn- AND ^{64}Zn-LABELLING

Margaret L. Niven and David A. Thornton

Department of Inorganic Chemistry
University of Cape Town, Rondebosch 7700, South Africa

ABSTRACT

The infrared spectrum of *bis*(acetylacetonato)zinc(II) monohydrate and its ^{18}O-, ^{68}Zn- and ^{64}Zn-labelled analogues have been determined. Band assignments have been made on the basis of the isotopically-induced shifts in relation to the C_{4v} localized point symmetry of the molecule. Unlike *tris*(acetylacetonato)chromium(III), there is no disagreement between the results of the ^{18}O and metal isotope labelling techniques.

INTRODUCTION

There are serious discrepancies between the assignments resulting from ^{18}O-labelling[1,2] and metal isotope ($^{53,50}Cr$) labelling[3] studies on the vibrational spectra of chromium(III) *tris*(acetylacetonate), [Cr(acac)$_3$]. The results of these studies and those employing normal coordinate treatments[4,5] are compared in Table 1.

TABLE 1

Frequencies (cm^{-1}), isotopically-induced shifts ($\Delta\nu$, cm^{-1}) and band assignments for $[Cr(acac)_3]$[a]

Band frequency				Method	Ref.
592	463	416	358		
oop ring def	ν(Cr-O)	oop ring def	ν(Cr-O)	nct	4
oop ring def	ν(Cr-O) + δ(C-CH_3)	ring def	ν(Cr-O)	nct	5
ν(Cr-O) $\Delta\nu$ =19[b]	ν(Cr-O) + δ(C-CH_3) $\Delta\nu$ = 5[b]	δ(O-Cr-O) $\Delta\nu$ = 8[b]	na	^{18}O-labelling	1
oop ring def $\Delta\nu$ = 0.7[c]	ν(Cr-O) $\Delta\nu$ = 3.0[c]	oop ring def $\Delta\nu$ = 0[c]	ν(Cr-O) $\Delta\nu$ = 3.9[c]	$^{53,50}Cr$-labelling	3
ν(Cr-O) $\Delta\nu$ = 19[b]	ν(Cr-O) + δ(C-CH_3) $\Delta\nu$ = 10[d]	ip δ(O-Cr-O) $\Delta\nu$ = 5[d]	ip δ(C-C-C) $\Delta\nu$ = 2[d]	^{18}O-labelling	2

[a] Abbreviations: oop = out-of-plane, def = deformation, nct = normal coordinate treatment, na = not assigned, ip = in-plane.

[b] Shift in infrared band on ^{18}O-labelling.

[c] Difference in frequencies between ^{53}Cr- and ^{50}Cr-labelled species.

[d] Shift in Raman band on ^{18}O-labelling.

One would expect that the vibrationally-purest ν(Cr-O) band would exhibit maximum shift on both ^{18}O- and $^{53,50}Cr$-labelling. In practice, the 592 cm^{-1} band shifts most on ^{18}O-labelling while the 358 cm^{-1} band shifts most on $^{53,50}Cr$-labelling.

We have now examined the effects of both ^{18}O- and $^{68,64}Zn$-labelling on the infrared spectrum of $[Zn(acac)_2(H_2O)]$ in order to determine whether mutually contradictory assignments were observed for this complex also. The zinc complex was studied because the availability of the ^{68}Zn and ^{64}Zn isotopes represents an isotopic pair with sufficient mass difference to yield reasonable $^{68,64}Zn$-induced shifts.

EXPERIMENTAL

Zinc acetylacetonate monohydrate was prepared by the reported method.[6] The ^{18}O-, ^{64}Zn- and ^{68}Zn-labelled analogues were similarly prepared from ^{18}O-acetylacetone of 72% isotopic purity, $^{64}ZnSO_4$ of-98.6% isotopic purity and $^{68}ZnSO_4$ of 97.6% isotopic purity supplied by BOC Prochem Ltd. Spectra were determined on nujol mulls between caesium iodide plates (or, below 300 cm^{-1}, between polyethylene plates) on Beckman IR-12 and Perkin-Elmer 180 spectrophotometers. The purity of all compounds was determined by microanalysis (C, H).

RESULTS AND DISCUSSION

The frequencies, isotopically-induced shifts and assignments are given in Table 2.

TABLE 2

Frequencies, isotopically-induced shifts ($\Delta\nu$) and band assignments in the infrared spectrum of $[Zn(acac)_2(H_2O)]$.

Frequency (cm^{-1})	$\Delta\nu$ (cm^{-1})		Assignment
	^{18}O	$^{68,64}Zn$[a]	
3300			ν(C-H)
2966			ν(C-H)
2927			ν(C-H)
1599	2		ν(C=O)
1522	1		ν(C=C + ν(C=O)
1513	4		ν(C=O) + δ(C-H)
1453			δ(C-H)
1400			$\delta(CH_3)$ deg. def.
1370			$\delta(CH_3)$ sym. def.
1264			ν(C-C) + $\nu(C\text{-}CH_3)$
1191			δ(C-H) in-phase
1020			$\delta(CH_3)$ rock
933	1		$\delta(C\text{-}CH_3)$ + ν(C=O)
779			δ(C-H) out-of-plane
772			δ(C-H) out-of-plane
656		1	ring def.
570		1	ring def.
557	3	2	$\nu(Zn\text{-}O)$ + $\delta(C\text{-}CH_3)$
439	1	2	$\nu(Zn\text{-}OH_2)$
422	1		δ(C-C-C) in-plane
413	5	6	$\nu(Zn\text{-}O)$
388	1	1	δ(O-Zn-O) in-plane
241	6	5	δ(O-Zn-O) out-of-plane
208			δ(C-C-C) out-of-plane
173	1	3	$\delta(O\text{-}Zn\text{-}OH_2)$

[a] Difference between frequencies of ^{68}Zn- and ^{64}Zn-labelled compounds

The 4000 - 560 cm^{-1} region

Only four bands exhibit ^{18}O-sensitivity in this region of the spectrum, suggesting that each has a component of ν(C=O). These correspond precisely with those four bands for which ν(C=O) provides a contribution in the assignments previously obtained on the basis of normal coordinate analysis.[4] The ^{18}O-induced shifts are rather small compared with those observed[1] for [Cr(acac)$_3$], suggesting a greater degree of vibrational coupling in the Zn(II) complex. The remaining assignments are based on normal coordinate analyses of Cu(II) and metal(III) acetylacetonates.[4,5]

The 560 - 150 cm^{-1} region

Two bands (at 413 and 241 cm^{-1}) exhibit maximum ^{18}O-sensitivity. Moreover, as would be expected, the same two bands exhibit maximum sensitivity to metal isotope substitution. The band at higher frequency (413 cm^{-1}) is firmly assigned to ν(Zn-O) while that at 241 cm^{-1} is assigned to δ(O-Zn-O).

The C_{4v} localized point symmetry of [Zn(acac)$_2$(H$_2$O)], which has been crystallographically shown [6,7] to have approximate square based pyramidal coordination, implies the existence of six infrared-active metal-ligand modes: $2a_1 + e$ stretches and $a_1 + 2e$ bends of which two ν(Zn-O) and one ν(Zn-OH$_2$) stretches and two δ(O-Zn-O) and one δ(O-Zn-OH$_2$) bends are expected. The band at 557 cm^{-1} is logically assigned, on the grounds of its ^{18}O- and $^{68,64}Zn$-sensitivities, to the second ν(Zn-O) stretch, while the 439 cm^{-1} band is probably ν(Zn-OH$_2$). The 388 cm^{-1} and 173 cm^{-1} bands are assigned to δ(O-Zn-O), one of them involving the water molecule.

Comparison of the assignments in $[Cr(acac)_3]$ *and* $[Zn(acac)_2(H_2O)]$

Two features of $[Cr(acac)_3]$ suggest that ν(Cr-O) in this complex would be considerably higher than ν(Zn-O) in $[Zn(acac)_2(H_2O)]$. One is the crystal field stabilization energy (cfse) effect[8]. On this basis, the high cfse of the Cr(III) complex (12 *Dq*) would raise ν(Cr-O) well above ν(Zn-O), since the Zn(II) complex has zero cfse. The second feature is the oxidation state effect[9] which would again yield ν(Cr-O) > ν(Zn-O). On the other hand, these effects will be offset to some extent by the lower coordination number of the zinc(II) ion in $[Zn(acac)_2(H_2O)]$. Overall, it seems likely that ν(Cr-O) will exceed ν(Zn-O), favouring the assignment of the 592 cm^{-1} band to ν(Cr-O) rather than the 358 cm^{-1} band.

ACKNOWLEDGEMENTS

We thank the University Research Committee and the Council for Scientific and Industrial Research for financial assistance.

REFERENCES

1. S. Pinchas, B.L. Silver and I. Laulicht, *J. Chem. Phys.*, *46*, 1506 (1967)
2. S. Pinchas and J. Shamir, *J. Chem. Soc. Perkin II*, 1098 (1974).
3. K. Nakamoto, C. Udovich and J. Takemoto, *J. Amer. Chem. Soc.*, *92*, 3973 (1970).
4. K. Nakamoto, P.J. McCarthy, A. Ruby and A.E. Martell, *J. Amer. Chem. Soc.*, *83*, 1066 (1961).
5. M. Mikami, I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, *23A*, 1037 (1967).

6. E.L. Lippert and M.R. Truter, *J. Chem. Soc.*, 4996 (1960).

7. H. Montgomery and E.C. Lingafelter, *Acta Cryst.*, *16*, 748 (1963).

8. R.D. Hancock and D.A. Thornton, *J. Mol. Struct.*, *4*, 361 (1969).

9. L.G. Hulett and D.A. Thornton, *J. Inorg. Nucl. Chem.*, *35*, 2661 (1973).

Received: March 21, 1980
Accepted: April 16, 1980