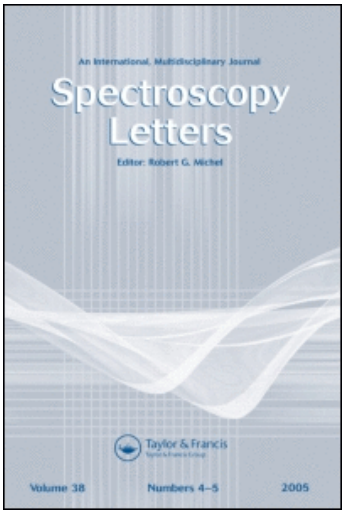

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Vibrational Spectra of $[Zn(^{15}NH_3)_4]$ $(ReO_4)_2$ and $[Cd(NH_3)_4]$ $(ReO_4)_2$ With $^{110}Cd/^{116}Cd$ and H/D Isotopic Substitution

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To cite this Article Tellez, Claudio(1988) 'Vibrational Spectra of $[Zn(^{15}NH_3)_4]$ $(ReO_4)_2$ and $[Cd(NH_3)_4]$ $(ReO_4)_2$ With $^{110}Cd/^{116}Cd$ and H/D Isotopic Substitution', Spectroscopy Letters, 21: 8, 871 — 878
To link to this Article: DOI: 10.1080/00387018808082349
URL: http://dx.doi.org/10.1080/00387018808082349

SPECTROSCOPY LETTERS, 21(8), 871-878 (1988)

VIBRATIONAL SPECTRA OF $[Zn(^{15}NH_3)_4](ReO_4)_2$ AND $[Cd(NH_3)_4](ReO_4)_2$ WITH $^{110}Cd/^{116}Cd$ AND H/D ISOTOPIC SUBSTITUTION.

Key words : Vibrational spectra , Zn , Cd isotopic ammin complexes .

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ABSTRACT : The infrared spectra of the zinc tetraammine with ^{15}N , and cadmium tetraammine perrhenates with $^{110}Cd/^{116}Cd$ and H/D isotopic substitution , provides useful data in determining skeletal pseudo - exact force constants . An approximate set of force constants in the F_2 symmetry class for the whole complexes were obtained .

INTRODUCTION

We sintetized and measured the spectra of $[Zn(^{15}NH_3)_4](ReO_4)_2$, $[Cd(ND_3)_4](ReO_4)_2$, $[^{110}Cd(NH_3)_4]$

$(ReO_4)_2$ and $[^{116}Cd(NH_3)_4](ReO_4)_2$ and remeasured those corresponding to $[Zn(NH_3)_4](ReO_4)_2$ and $[Cd(NH_3)_4](ReO_4)_2$. All the complexes studied in this work are isostructural (1,2), crystallize in the cubic space group T_d^2- $F\bar{4}3m$ with Z = 4 , and contain the same anion .

A normal ccordinate analysis was carried out based on a modified valence force field.

EXPERIMENTAL DETAILS

The method used to prepare the ammine complexes of Zn(II) and Cd(II) , corresponds roughly to that reported in literature (3,4) but on a mg scale.

The infrared spectra of the nujol mulls of the complexes were measured on a Perkin-Elmer IR-180 Spectrometer . The Raman spectra were recorded on a Coderg Laser Raman Spectrometer PHO using an Ar^+ laser from Spectra-Physics (exitation line : 5145 Å). The calibration was made using water vapour and the Ar^+ plasma line (5).

NORMAL COORDINATE ANALYSIS: Following Cyvin's rule (7) , the vibrations may be classified as due to (i) ligand , (ii) ligand-framework coupling and (iii) skeletal vibrations.

The set of symmetry coordinates employed in the present calculations is the same as the one reported by Cyvin, et al. (8). Bond lengths of 2.01 Å, 2.10 Å and 1.01 Å were assumed for the Zn-N, Cd-N and N-H bonds,

TABLE 1. Infrared and Raman Spectra of the $[Zn(^{15}NH_3)_4](ReO_4)_2$ and $[Cd(NH_3)_4](ReO_4)_2$ complexes with deuterium and $^{110}Cd/^{116}Cd$ isotopic substitution (in cm^{-1}).

IR.spectra	$[Zn(^{15}NH_3)_4](ReO_4)_2$	$[^*Cd(NH_3)_4](ReO_4)_2$	$[Cd(ND_3)_4](ReO_2)_2$
ν_{as}(NH)	3319.0 ± 2.0(s)	3352.5 ± 2.0(s)	2501.0 ± 5.0(s)
ν_s(NH)	3259.0 ± 2.0(w)	3266.5 ± 1.0(w)	2378.0 ± 2.0(w)
$2\delta_{as}$(HNH) (**)	3174.0 ± 2.0(w)	3184.0 ± 2.0(w)	2321.0 ± 2.0(w)
δ_{as}(HNH)	1618.0 ± 2.0(s)	1617.0 ± 2.0(s)	1182.5 ± 2.0(s)
δ_s(HNH)	1237.5 ± 1.0(w)	1175.0 ± 2.0(w)	- -
$\rho_r(NH_3)$	714.0 ± 2.0(m)	670.0 ± 2.0(m)	502.0 ± 3.0(m)
ν_{as}(MN)	403.5 ± 0.3(w)	371.0 ± 0.2(w) (a)	348.0 - 1.0
		372.0 ± 0.5(w) (b)	
δ_{as}(NMN)	188.5 ± 0.8(m)	167.5 ± 0.3(m) (a)	155.0 ± 2.0(m)
		167.5 ± 0.3(m) (b)	
Raman spectra: Framework frequencies.			
ν_s(MN)	411.0 ± 3.0(w)	387.0 ± 1.0(w) (a,b)	360.0 ± 1.0(w)
δ_s(NMN)	174.5 ± 4.0(w)	162.5 ± 4.0(w) (a,b)	146.0 ± 2.0(w)

(a) ^{110}Cd and (b) ^{116}Cd labeled ammine complexes

(**) overtone or combination bands

RESULTS AND DISCUSSION

VIBRATIONAL SPECTRA: Since the Zn and Cd tetraammine perrhenate complexes are isostructural, their spectra are analogous. The fundamentals can be classified acording to the species: $\Gamma = 3A_1(R) + A_2(-) + 4E(R) + 4F_1(-) + 7F_2(IR, R)$, where all the IR. active fundamentals could be observed.

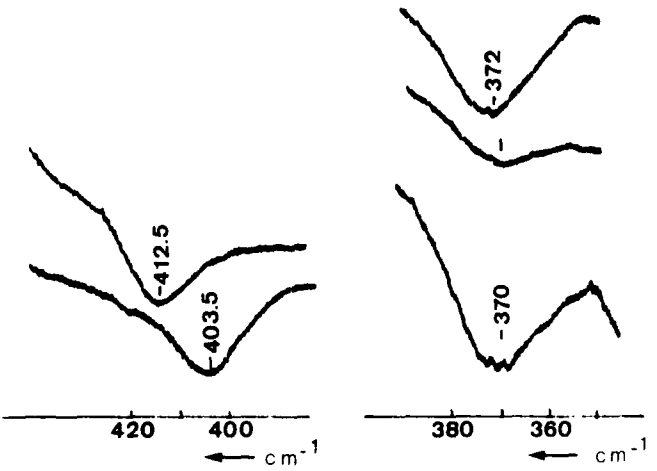

Fig.1.Metal ligand ν_{as}(MN) IR skeletal stretching bands: A) $[Zn(NH_3)_4](ReO_4)_2$,B) $[Zn(^{15}NH_3)_4](ReO_4)_2$, C) $[^{110}Cd(NH_3)_4](ReO_4)_2$,D)$[^{116}Cd(NH_3)_4](ReO_4)_2$

In the Raman spectrum of $[Zn(^{15}NH_3)_4](ReO_4)_2$, two bands for the skeletal vibrations were observed. These vibrations, which occur at 411.0 $\pm$ 3.0 cm^{-1} and 174.5 $\pm$ 4.0 cm^{-1}, correspond to the ν_s(ZnN) and δ_s(NZnN) modes in the A_1 and E species, respectively. The Raman spectrum of the $^{110}Cd/^{116}Cd$ central atom substituted ammine complexes shows, in the region of skeletal vibrations , the same two bands observed for the Zn complex . For $[^{110}Cd(NH_3)_4](ReO_4)_2$ and $[^{116}Cd(NH_3)_4](ReO_4)_2$, these bands appear at 387.0 $\pm$ 1.0 cm^{-1} and 162.5 $\pm$ 4.0 cm^{-1} , respectively. For the $[Cd(ND_3)_4](ReO_4)_2$ complex we reported the H/D shift of 27.0 $\pm$ 2.0 cm^{-1} for the ν_s(CdN) (A_1) symmetric stretching mode. For the bending δ_s(NCdN)

TABLE 2.-SYMMETRY FORCE CONSTANTS FOR THE MX_4 SKELETONS: ($X=NH_3$; M= Zn , Cd) (mdyn/Å)

		isotopic substitution*	
$[Zn(NH_3)_4]^{2+}$		$^{14}N/^{15}N$	
$F_{11}(A_1) \cong F_{(MN)s}$	1.79 ± 0.02 [a]		
$F_{33}(F_2) \cong F_{(MN)as}$		1.34 ± 0.05	
$F_{34}(F_2) \cong F_{(MN/NMN)}$		0.11 ± 0.06	
$F_{44}(F_2) \cong F_{(NMN)as}$		0.13 ± 0.03	
$[Cd(NH_3)_4]^{2+}$		isotopic substitution $^{14}N/^{15}N$	$^{110}Cd/^{116}Cd$
$F_{11}(A_1) \cong F_{(MN)s}$	1.50 ± 0.01 [a]		
$F_{33}(F_2) \cong F_{(MN)as}$		1.19 ± 0.06	1.14 ± 0.08
$F_{34}(F_2) \cong F_{(MN/NMN)}$		0.11 ± 0.10	0.00 ± 0.07
$F_{44}(F_2) \cong F_{(NMN)as}$		0.11 ± 0.03	0.11 ± 0.01

(a) Determined by taking $\nu_s(ZnN)(A_1)$ and $\nu_s(CdN)(A_1)$ from the Raman spectra of solid $[Zn(^{15}NH_3)_4](ReO_4)_2$ and $[^{110}Cd(NH_3)_4](ReO_4)_2$.

(b) See ref .(11). (*) Natural abundance of ^{14}N is about 99.634%.

Table 3 . Symmetry force constants (F_2 symmetry species) (mdyn/Å) for the complexes $[M(NH_3)_4](ReO_4)_2$; M= Zn , Cd .

		$[Zn(NH_3)_4]^{2+}$	$[Cd(NH_3)_4]^{2+}$
	initial set	final set	final set
$F_{(NH)} \cong F_{11}$	6.48	6.19 ± 0.03	6.30 ± 0.18
F_{12}	0.42	0.41 ± 0.03	0.41 ± 0,12
$F_{(HNH)s} \cong F_{22}$	0.48	0.79 ± 0.00	0.70 ± 0.00
$F_{(NH)as} \cong F_{33}$	6.45	6.02 ± 0.03	6.16 ± 0.18
F_{34}	-0.16	-0.16 ± 0.06	-0.15 ± 0.30
$F_{(HNH)as} \cong F_{44}$	0.59	0.58 ± 0.00	0.58 ± 0.01
$F_{(NH_3)r} \cong F_{55}$	0.13	0.15 ± 0.06	0.13 ± 0.02
$F_{(MN)as} \cong F_{66}$	1.34 ; 1.19*	1.37 ± 0.01	1.23 ± 0.03
F_{67}	0.11 ; 0.11*	0.11 ± 0.00	0.10 ± 0.02
$F_{(NMN)as} \cong F_{77}$	0.13 ; 0.11*	0.14 ± 0.01	0.12 ± 0.01
	valence force constants		
$f_{(NH)}$	6.46	6.04	6.21
$f_{(NH/NH)}$	0.01	0.02	0.04
$f_{(MN)}$		1.45 ± 0.03	1.25 ± 0.05
$f_{(MN/MN)}$		0.11 ± 0.02	0.09 ± 0.02

(*) See Table 2.

(a) The valence force constants were obtained through the analytical expressions of the symmetry force constants: (a) Ligands:

$$F_{11} = f_{(NH)} + 3\, f_{(NH/NH)}$$

$$F_{33} = f_{(NH)} - f_{(NH/NH)}$$

(b) Framework :

$$F_{(MN)_s}(A_1) = f_{(MN)} + 3\, f_{(MN/MN)}$$

$$F_{(MN)_{as}}(F_2) = f_{(MN)} - f_{(MN/MN)}$$

mode the H/D shift was found to be 16.5 ± 6.0 cm^{-1} (6). Table 1, includes the infrared and Raman spectra of the Cd and Zn ammine perrhenate complexes. The isotopic shifts for the $\nu_{as}(MN)$ (F_2) IR. active skeletal modes for the Zn and Cd isotopic complexes are shown in Figure 1.

For the former, in a similar manner to Cyvin and co-workers (7,9), it was assumed that the interaction force constants between different NH_3 groups, and between the framework and the NH_3 ligands, were equal to zero. For the NH_3 ligands, the initial set of force constants were taken from reference (9). The ligand-frame work coupling initial force constant was obtained from the relation $F_{ii}=\lambda_i G_{ii}^{-1}$, were obtained based on the point mass model approximation (10) and are collected in Table 2. The calculations were performed by Wilson's GF matrix method and the final set of force constants $F(F_2)$ are listed in Table 3.

ACKNOWLEDGEMENTS

Thanks are due to CNPq (Brasil). Proc. Nº. 402738/85-QU.

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Date Received: 04/05/88
Date Accepted: 05/09/88