

# METAL LIGAND VIBRATIONS OF $[Cd(NH_3)_4](ReO_4)_2$ WITH $^{110}Cd/^{116}Cd$ AND H/D ISOTOPIC SUBSTITUTION

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## ABSTRACT

Raman and ir. Spectra of  $[Cd(NH_3)_4](ReO_4)_2$  with  $^{110}Cd/^{116}Cd$  and H/D isotopic substitution have been obtained. The frequencies and isotopic shift for the framework of the  $[Cd(NH_3)_4]^{2+}$  cation complex are reported.

## INTRODUCTION

Raman spectra of  $[Cd(NH_3)_4](ReO_4)_2$  and with  $^{15}N$  isotopic substitution was previously reported<sup>(6)</sup>. Up to date, the isotopic shifts  $^{110}Cd/^{116}Cd$  and H/D for the tetraamminecadmium (II) perrhenate complex were not informed. The Raman spectrum of  $[Zn(NH_3)_4]I_2$  with  $^{14}N/^{15}N$ ,  $^{64}Zn/^{68}Zn$  and H/D isotopic substitutions has been published in<sup>(3,5)</sup>. In the Raman spectrum of  $[Co(NH_3)_4](ReO_4)_2$  only one band pertaining to the cation complex was observed<sup>(2)</sup>.

In the present work the ir. and Raman skeletal frequencies and isotopic shifts for the tetraamminecadmium (II) perrhenate complex are reported.

## EXPERIMENTAL

The method followed for the preparation of the cadmium tetraammine complexes corresponds roughly to that one reported in the literature<sup>(1,8)</sup>. This methods leads to a high yield of metal perrhenates but is suited only for large quantities. To work with small quantities of the substances, the following procedures were adopted: Solutions of  $CdCl_2$  were treated with stoichiometric quantities of solid  $AgReO_4$  in suspension and gaseous ammonia was passed through the filtered solution of the above reaction products. The derived complexes were dried over KOH.

$^{110}CdCl_2$  and  $^{116}CdCl_2$  were obtained reacting  $^{110}Cd$  and  $^{116}Cd$  with HCl. In the synthesis of the

labeled complexes, in each case 100mg. of solid  $AgReO_4$  and corresponding stoichiometric quantities of  $CdCl_2$  were allowed to react in minimum possible volume of the solutions.

$[Cd(ND_3)_4](ReO_4)_2$  was prepared using deuterated water and deuterated ammonia. The entire preparation was carried out in Ar Atmosphere.

The Raman spectra of the above mentioned compounds were scanned with a Coderg Raman laser spectrometer PHO using a  $Ar^+$  laser from Spectra-Physics (excitation line 514.5 nm). The ir. spectra (Nujol mulls) were recorded on a Perkin-Elmer IR-180 Spectrometer. The calibration was made according to standard tables<sup>(7)</sup>.

## RESULTS AND DISCUSSION

The normal modes for the  $[MX_4]^{2+}$  framework ( $X=NH_3$ ), in a  $T_d$  symmetry can be represented by:

$$\Gamma(T_d) = a_1(R) + e(R) + 2f_2(IR,R)$$

In the Raman spectra, in the 450 - 100  $cm^{-1}$  region, in addition to the anion band, two bands were observed (see Table I) which can be assigned to  $\nu_s(CdN)$  ( $a_1$ ) and  $\delta_s(NCdN)$  ( $e$ ), respectively.

Theoretically, the H/D skeletal isotopic shifts are expected to be observed for all the three symmetry species. In the ( $a_1$ ) and ( $e$ ) species, the analy-

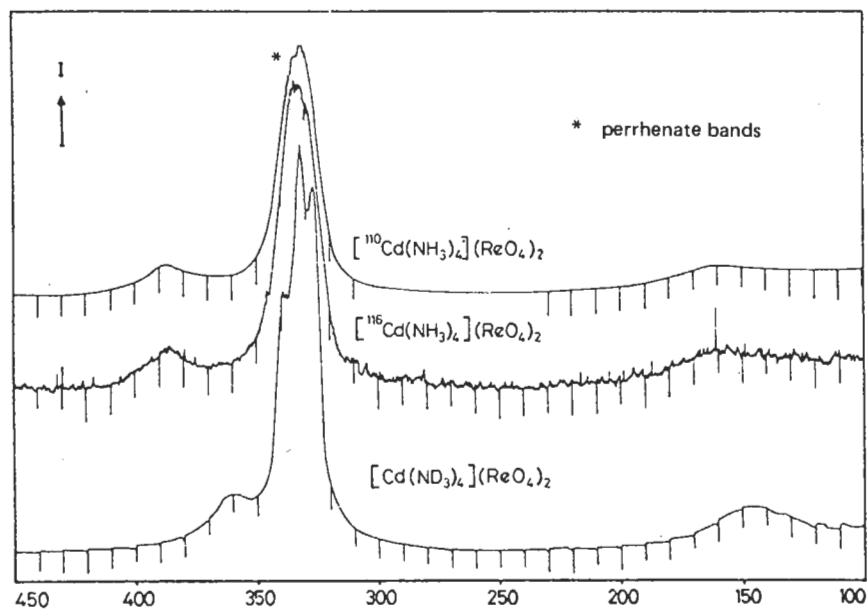


Fig. I. Raman spectra of  $[Cd(NH_3)_4](ReO_4)_2$  in the region of the skeletal vibrations.

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tical expressions for the G matrix do not include the metal reciprocal mass, giving identical values of the kinematic matrix elements for the  $^{110}\text{Cd}$  and  $^{116}\text{Cd}$  isotopic tetraammine complexes. Therefore, according to the Teller-Redlich product rule<sup>(4)</sup>, the frequency

ratio for the metal labeled complexes is equal to unity.

The uncertainty in the determination of the isotopic shifts for  $\delta_s(\text{NCdN})$  (e) is due to the breadth and weakness of the bands.

The Raman spectra are illustrated in Figure I. Table I includes the  $^{110}\text{Cd}/^{116}\text{Cd}$  and H/D frequency shifts measured in the ir. spectra. The bands for the  $f_2$  species were not observed in the Raman spectra.

Table I. FRAMEWORK FREQUENCIES AND ISOTOPIC SHIFTS ( $\text{cm}^{-1}$ ) FOR  $[\text{Cd}(\text{NH}_3)_4]^{2+}$ .

Species	$\nu_1(a_1) \hat{=} \nu_s(\text{CdN})$	$\nu_2(e) \hat{=} \delta_s(\text{NCdN})$	$\nu_3(f_2) \hat{=} \nu_{as}(\text{CdN})$	$\nu_4(f_2) \hat{=} \delta_{as}(\text{NCdN})$
$[^{110}\text{Cd}(\text{NH}_3)_4]^{2+}$	387.0 $\pm$ 1.0 (R)	162.5 $\pm$ 4.0 (R)	372.0 $\pm$ 0.3 (IR)	167.5 $\pm$ 0.3 (IR)
$[^{116}\text{Cd}(\text{NH}_3)_4]^{2+}$	387.0 $\pm$ 1.0 (R)	162.5 $\pm$ 4.0 (R)	370.0 $\pm$ 0.5 (IR)	167.0 $\pm$ 0.3 (IR)
$[\text{Cd}(\text{ND}_3)_4]^{2+}$	360.0 $\pm$ 1.0 (R)	146.0 $\pm$ 2.0 (R)	348.0 $\pm$ 1.0 (IR)	155.0 $\pm$ 2.0 (IR)
Isotopic shifts				
	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_3$	$\Delta\nu_4$
$^{110}\text{Cd}/^{116}\text{Cd}$	0.0 (R)	0.0 (R)	2.0 $\pm$ 0.8 (IR)	0.5 $\pm$ 0.6 (IR)
H/D	27.0 $\pm$ 2.0 (R)	16.5 $\pm$ 6.0 (R)	23.0 $\pm$ 2.0 (IR)	12.5 $\pm$ 2.3 (IR)

#### RESUMO

Obtenção dos espectros Raman e Infravermelho do Complexo  $[\text{Cd}(\text{NH}_3)_4](\text{ReO}_4)_2$  com substituição isotópica  $^{110}\text{Cd}/^{116}\text{Cd}$  e H/D. Informação das frequências e deslocamentos isotópicos do esqueleto do cátion  $[\text{Cd}(\text{NH}_3)_4]^{2+}$ .

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