

The Low Frequency IR and Raman Spectra of Some Complexes of Dithiooxamide with Cadmium Halides

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Summary. The low frequency IR and Raman spectra of $\text{Cd}(\text{DH}_4)\text{X}_2$ ($X = \text{Cl}, \text{Br}$; DH = dithiooxamide) have been discussed. On the basis of the cadmium isotope and H-D shift as well as chlorine-bromine substitution a band assignment in the region $500\text{--}33\text{ cm}^{-1}$ has been made. A polymeric structure of $\text{Cd}(\text{DH}_4)\text{X}_2$ involving both dithiooxamide and halogen bridges with D_{4h} symmetry of the cadmium environment is assumed.

Keywords. Cadmium(II); Dithiooxamide; Isotope substitution; Vibrational spectroscopy.

Die niederfrequenten IR- und Raman-Spektren einiger Komplexe von Dithiooxamid mit Cadmiumhalogeniden

Zusammenfassung. Die IR- und Raman-Spektren von $\text{Cd}(\text{DH}_4)\text{X}_2$ ($X = \text{Cl}, \text{Br}$; DH = Dithiooxamid) werden im Bereich niedriger Frequenzen diskutiert. Basierend auf Cadmiumisotopen- und H-D-Verschiebungen mit zusätzlicher Cl-Br-Substitution werden die Banden im Bereich von $500\text{--}33\text{ cm}^{-1}$ zugeordnet. Es wird eine polymere Struktur von $\text{Cd}(\text{DH}_4)\text{X}_2$ unter Anteilnahme sowohl von Dithiooxamid- als auch Halogenbrücken mit einer D_{4h} -Symmetrie im Bereich des Cadmiumzentrations angenommen.

Introduction

Dithiooxamide DH_4 , a very weak acid, can form different types of metal complexes depending on the pH of the solution [1–10]. In acidic solution DH_4 acts as a neutral ligand and gives cationic $[\text{M}(\text{DH}_4)_2]\text{X}_2$ complexes with some transition metals [2–4]. It has been reported that in neutral or basic media dithiooxamide functions as divalent anion and forms 1 : 1 N,S-coordinated polymeric compounds with Ni, Co, Pt, Pd, Zn [1, 5–7, 9, 10].

Only cadmium and mercury are known to form complexes of the type $\text{M}(\text{DH}_4)\text{X}_2$ where $X = \text{Cl}, \text{Br}$ in neutral or acidic solution [8]. Pellacani and coworkers [8] have studied the IR spectra and molar conductivities of these complexes.

In order to determine the structure of the inner coordination sphere of the $\text{Cd}(\text{DH}_4)\text{X}_2$ complexes, the low frequency region of IR and Raman spectra has been studied in this work.

Experimental

$\text{Cd}(\text{DH}_4)\text{Cl}_2$ was prepared by two ways: (a) in acidic solution, by the method described previously by Pellacani [8], and (b) in neutral media; an ethanolic solution of dithiooxamide was added to an aqueous solution of CdCl_2 . The complexes obtained by both methods had the same composition and properties. Anal. found: C 8.08, N 9.20, Cl 22.60%; calc.: C 7.99, N 9.24, Cl 23.40%.

$\text{Cd}(\text{DH}_4)\text{Br}_2$ was obtained in the same way as its chlorine analogue using CdBr_2 and HBr solutions; anal. found: C 6.68, N 7.18, Br 38.10%; calc.: C 6.18, N 7.14, Br 40.50%.

$\text{Cd}(\text{DH}_4\text{-}d_4)\text{Cl}_2$ dithiooxamide- d_4 was prepared by recrystallizing dithiooxamide from *EtOD* several times. Hydrated CdCl_2 was recrystallized from D_2O . The complex was synthesized using the same method as described above, but D_2O , DCl and *EtOD* were used as solvents.

$^{114}\text{Cd}(\text{DH}_4)\text{Cl}_2$ and $^{112}\text{Cd}(\text{DH}_4)\text{Cl}_2$ were prepared on a milligram scale using stable isotopes of cadmium.

The IR spectra were measured using Perkin-Elmer 621 ($4000\text{--}200\text{ cm}^{-1}$) and Hitachi-Perkin-Elmer FIS3 ($410\text{--}33\text{ cm}^{-1}$) spectrophotometers by standard techniques. The Raman spectra were recorded on a Jeol IRS-S1 laser Raman spectrophotometer, using the 488.8 nm line of an Ar^+ laser as excitation source. To avoid sample decomposition the rotating disc technique was applied.

Results and Discussion

Pellacani and coworkers [8] have presented some characteristic bands of the IR spectra of $\text{Cd}(\text{DH}_4)\text{X}_2$ complexes. However, the spectra were measured down to 160 cm^{-1} in that investigation and a number of bands were left unassigned. Table 1 lists the frequencies observed in this work for the cadmium chloride complex, its deuterated analogue, dithiooxamide and dithiooxamide- d_4 as well as Pellacani's results [8].

The spectrum of the $\text{Cd}(\text{DH}_4)\text{Cl}_2$ complex in the region of the ligand vibrations (above 500 cm^{-1}) is very similar to the spectrum of the solid DH_4 with respect to the frequencies, intensities and even the band shapes (Fig. 1). Therefore it is rather obvious that the ligand configuration does not change due to complexation and that the symmetry of dithiooxamide remains unaltered. The solid DH_4 has a trans-planar structure [11]. Assuming the same structure of dithiooxamide in its cadmium chloride complex the IR bands with the maxima above 470 cm^{-1} have been assigned

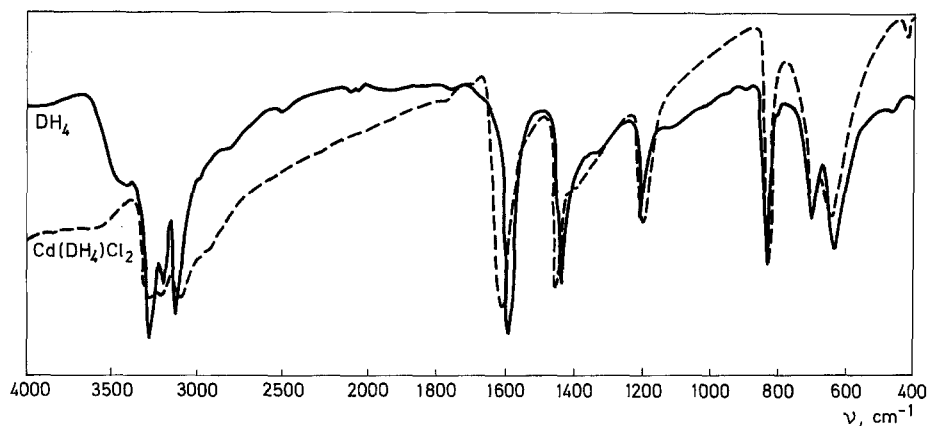


Fig. 1. The IR spectrum of dithiooxamide and its cadmium chloride complex in the region $4000\text{--}400\text{ cm}^{-1}$

Table 2. IR and Raman bands [cm^{-1}], isotope shifts and band assignments for CdLX_2 type complexes ($L = \text{DH}_4 = \text{dithiooxamide}$)

No.	IR ^a		Raman ^b							Δ_4	Assignment
	$^{112}\text{CdLCl}_2$	Δ_1	$^{NA}\text{CdL}_{d4}\text{Cl}_2$	Δ_2	$^{NA}\text{CdLBr}_2$	Δ_3	$^{NA}\text{CdLCl}_2$	$^{NA}\text{CdLBr}_2$			
ν_1	—	—	469	1	488	— 14	—	—	—	lig. vibr.	
ν_2	399	1	371	26	—	—	—	360	—	lig. vibr. + $\nu(\text{Cd—S})$	
ν_3	330	2	317	11	323	5	325	—	—	$\nu(\text{Cd—S})$	
ν_4	203	—	203	—	149	54	208	164	44	$\nu(\text{Cd—X})$	
ν_5	163	4	159	—	117	42	160	112	38	$\delta(\text{X—Cd—X})$	
ν_6	123	5	120	— 2	95	23	110	—	—	$\delta(\text{X—Cd—S})$	
ν_7	69	1	64	3	57	11	—	—	—	lig. vibr. + $\delta(\text{X—Cd—S})$	

^a $\Delta_1 = \nu(^{112}\text{Cd}(\text{DH}_4)\text{Cl}_2 - \nu(^{114}\text{Cd}(\text{DH}_4)\text{Cl}_2)$; $\Delta_2 = \nu(^{114}\text{Cd}(\text{DH}_4)\text{Cl}_2 - \nu(^{NA}\text{Cd}(\text{DH}_4-d_4)\text{Cl}_2)$; $\Delta_3 = \nu(^{114}\text{Cd}(\text{DH}_4)\text{Cl}_2 - \nu(^{NA}\text{Cd}(\text{DH}_4)\text{Br}_2)$; NA—natural abundance

^b $\Delta_4 = \nu(^{NA}\text{Cd}(\text{DH}_4)\text{Cl}_2 - \nu(^{NA}\text{Cd}(\text{DH}_4)\text{Br}_2)$

on the basis of normal coordinate analysis carried out for pure DH_4 and DH_4-d_4 by Sathyanarayana [7].

The little augmentation of the nitrogen-carbon stretching frequency, from 1430 cm^{-1} to 1445 cm^{-1} and a slight decrease of the $\nu(\text{C-S})$ wavenumber from 840 cm^{-1} to 835 cm^{-1} caused by ligand complexation suggest the S,S-coordination of the DH_4 to the cadmium ion. This conclusion is also supported by the practically unchanged energies of stretching and bending modes of the NH_2 -group. Such a way of the ligand bonding is possible only in the case of bridging dithiooxamide. On this basis a polymeric structure is proposed for the complex.

In order to assign the band appearing in the IR and Raman spectra and to explain the complex structure, the following substitutions have been made: metal isotope substitution, halogen substitution, and deuteration of the ligand.

The low frequency vibrational spectra of the examined compounds and the isotope shifts are given in Table 2.

It is known, that vibrational bands caused by the metal-chlorine stretching vibration of the terminally bonded chlorides have a wavenumber about 50 cm^{-1} higher than those derived from the bridging chlorides [12]. The halogen-cadmium stretching frequencies observed for several N,S-coordinated complexes are collected in Table 3.

In the low frequency region of the $\text{Cd}(\text{DH}_4)\text{Cl}_2$ spectrum three bands are very sensitive to the halogen substitution, namely those at 203 , 159 and 118 cm^{-1} (ν_4 , ν_5 and ν_6). These bands shift to 149 , 117 and 95 cm^{-1} , respectively, after a Cl-Br change. The band located at 203 cm^{-1} in the $\text{Cd}(\text{DH}_4)\text{Cl}_2$ spectrum was assigned to

Table 3. The Cd—X stretching frequencies for bridging and the terminal cadmium-halogen bond (IR)

Compound	Frequency (cm^{-1})		Ref.
	Cd—X terminal	Cd—X bridging	
$\text{CdCl}_2(4\text{-aminobenzophenone})$		190	[13]
$\text{CdBr}_2(4\text{-aminobenzophenone})$		140	[13]
$\text{CdBr}_2(\text{dimethylacetamide})$	199		[14]
$\text{CdCl}_2(2,2'\text{-dimethylpropanediamine})$	274	170	[15]
$\text{CdBr}_2(2,2'\text{-dimethylpropanediamine})$	189	146	[15]
$\text{CdCl}_2(\text{imidazoline-2-thione})$	240		[16]
$\text{CdBr}_2(\text{imidazoline-2-thione})$	230		[16]
$\text{CdCl}_2(\text{pyridine})$		223	[17]
		216	
$\text{CdBr}_2(\text{pyridine})$		179	[17]
		173	
$\text{CdCl}_2(\text{tri-tert-butylphosphine})$	285	208	[18]
$\text{CdBr}_2(\text{tri-tert-butylphosphine})$	198	146	[18]
$\text{CdCl}_2(\text{aniline})$		223	[19]
		208	
$\text{CdBr}_2(\text{aniline})$		140	[19]
$\text{CdCl}_2(\text{dithiooxamide})$		203	this work
$\text{CdBr}_2(\text{dithiooxamide})$		149	

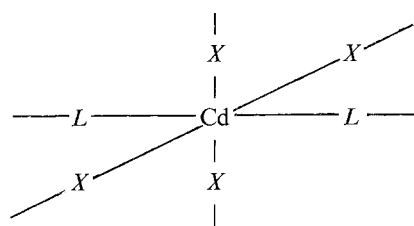


Fig. 2. The inner coordination sphere of the $\text{Cd}(\text{DH}_4)\text{Cl}_2$ complex

the stretching of the Cd—Cl bond. A $\nu_{\text{Br}}/\nu_{\text{Cl}}$ ratio equal to 0.73 confirms that this is predominately the $\nu(\text{Cd—Cl})$ mode [19]. The lack of the deuteration sensitivity of the ν_4 vibration also supports its cadmium-chlorine stretching character. As one can see from Table 3, the band discussed lies exactly in the frequency region characteristic for the vibration of the chlorine-cadmium bridging bond. In view of this fact it can be stated that the chlorides act as bridges in the complex. The appearance of two kinds of bridges (DH_4 and X) indicates a structure of the complex shown in Fig. 2. This complex contains a coordination skeleton of D_{4h} local symmetry.

The three lowest bands observed in the IR spectra of $\text{Cd}(\text{DH}_4)\text{X}_2$ (ν_5 , ν_6 and ν_7) are due to the deformation of the metal-ligand bonds. Thus, the band located at 159 cm^{-1} (IR) and $^{114}\text{Cd}(\text{DH}_4)\text{Cl}_2$ and at 117 cm^{-1} (IR) of $\text{Cd}(\text{DH}_4)\text{Br}_2$ (Cd of natural abundance) probably arises from the $X\text{-Cd-X}$ bending mode. This band shows the large isotope shift ($\Delta_1 = 4\text{ cm}^{-1}$), is very sensitive to halogen substitution ($\Delta_3 = 42\text{ cm}^{-1}$) but does not change its position after deuteration. The Cd(II) complex with aniline exhibits a similar band at 153 cm^{-1} with the chlorine-bromine shift equal 42 cm^{-1} [19]. In the IR spectrum of CdX_2L ($L = \text{aminobenzophenone}$, $X = \text{Cl, Br}$) the analogous bands were located at 147 cm^{-1} for chloro and at 121 cm^{-1} for the bromo analogues [13].

The ν_6 band in the spectra of $\text{Cd}(\text{DH}_4)\text{X}_2$ is very sensitive to the ^{114}Cd - ^{112}Cd substitution ($\Delta_1 = 5\text{ cm}^{-1}$) and to the halogen change ($\Delta_3 = 25\text{ cm}^{-1}$) but it shows a little shift after deuteration; it can be assigned as a $X\text{-Cd-S}$ deformation mode.

The shift observed for the ν_3 band (see Table 3) due to cadmium isotope substitution indicates that this band arises from Cd—S stretching vibration. The frequency of the ν_3 band decreases after deuteration by 11 cm^{-1} , which suggests a significant coupling of cadmium-sulphur stretching with the vibration of the neighbouring NH_2 -group. A similar vibration was observed between $281\text{--}342\text{ cm}^{-1}$ [20–22].

The assignment of the remaining IR bands is shown in Table 3.

The Raman spectra obtained in the $100\text{--}500\text{ cm}^{-1}$ region are shown in the Table 3 as well. The literature data concerning similar systems are rather scarce, except $\text{Cd}(\text{aniline})\text{Cl}_2$ [19] and $\text{Cd}(\text{2-methyl-5-mercapto-1,3,4-thiadiazole})\text{Cl}_2$ [21] spectra.

The band located at 325 cm^{-1} in the spectrum of $\text{Cd}(\text{DH}_4)\text{Cl}_2$ which is not observed for $\text{Cd}(\text{DH}_4)\text{Br}_2$ has been assigned to the Cd—S stretching mode. The analogical bands were located in the spectra of Cd(II) complexes with 1-methyl-5-mercaptopyperidine [20] and 2-methyl-mercapto-1,3,4-thiadiazole [21] at 275 cm^{-1} and 289 cm^{-1} , respectively.

The halogen substitution sensitive band, ν_4 , located at 208 cm^{-1} ($\Delta_4 = 44\text{ cm}^{-1}$) is probably due to the cadmium-chlorine stretching. This assignment is consistent with results given by Fabretti et al. [21].

Two lowest bands observed in the Raman spectrum at 160 cm^{-1} and 110 cm^{-1} are attributed to the deformation modes of the coordination bonds, namely to $\delta(\text{Cl—Cd—Cl})$ and $\delta(\text{Cl—Cd—S})$.

Conclusions

According to the infrared and *Raman* spectra combined with isotope substitution data, the examined complexes have been classified as inorganic polymers bridged both by halogen atoms as well as the dithiooxamide molecules. The analysis of the experimental data allows to assume a distorted octahedral symmetry of the cadmium environment. The position of the cadmium-ligand modes, especially the cadmium-chlorine and cadmium-bromine stretching vibrations have been established.

Acknowledgements

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