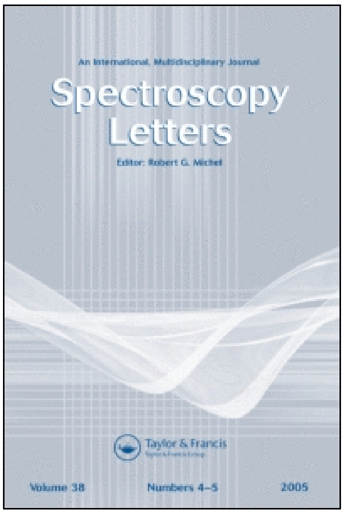

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The assignment of Co-C bond stretching vibrational frequency of $CH_3Co(DH)_2H_2O$ in IR and Raman spectra

KEY WORDS: Alkylcobaloxime, Normal Coordinate Analysis, IR, Raman

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ABSTRACT

In order to aid assignment of Co-C bond stretching vibrational frequency of $CH_3Co(DH)_2H_2O$ (DH=dimethylglyoximato monanion) in IR and Raman spectra, its isotopic substitution $CD_3Co(DH)_2H_2O$ has been synthesized and normal coordinate analyses on the two complex have been made. The bands were assigned in terms of potential energy distribution. The results provide definitive band assignment of the Co-C bond and Co-N bond stretching modes which are coupling at 511 cm^{-1}.

INTRODUCTION

As coenzyme B_{12} model complexes, the properties and spectra of the alkylcobaloximes have been extensive studied.[1] As well accepted homolysis of the Co-C bond is a key step in coenzyme B_{12} dependent enzyme catalytic cycle.[2,3] Therefore, definitive band assignment of Co-C stretching mode in alkylcobaloximes is important for elucidation of mechanism in B_{12}-dependent enzymatic reactions.

So far the assignment of Co-C bond stretching vibrational frequency of $RCo(DH)_2L$ (R=alkyl, L=H_2O or base) are quite controversial. For example, based on isotopic shift data in FT-Raman spectra, Nie et al.[4,5] assigned the Co-C stretching bands of $CH_3Co(DH)_2Py$ and $CH_3Co(DH)_2H_2O$ at 522 and 512 cm^{-1}, respectively. On the other hand, according to the ^{15}N-labeling IR spectra of $XCo(DH)_2Py$ (X=Cl, Br, I, CH_3), Rutherfod et al.[6] assigned Co-N (DH) and Co-C stretching bands of the complexes at near 510 and near 326 cm^{-1}, respectively. Which is in agreement with the assignment by Noboru Yamazaki et al.[7] The main purpose of our investigation is to provide definitive band assignment of Co-N(DH) and Co-C stretching bands of $CH_3Co(DH)_2H_2O$ based on normal coordinate analyses combined with isotopic shift data due to the $CD_3/CH_3Co(DH)_2H_2O$ substitution.

EXPERIMENTAL

The $CH_3Co(DH)_2H_2O$ complex was synthesized by reported method,[8] $CD_3Co(DH)_2H_2O$ was similarly prepared from CD_3I (99.85% isotopic purity, Aldrich). Infrared spectrum was obtained on a Brucker IF S66V spectrometer equipped with a DTGS detector for 4000-400 cm^{-1} region by the KBr pellet technique and a Nicolet 170 SX FT-IR Spectrometer equipped with a DTGS detector for the 500-100 cm^{-1} region by the Nujol mulls technique with polyethylene plates.

The Raman spectrum in the region 4000-100 cm^{-1} was measured on a Bruker KFS 100 spectrometer fitted with an InGaAs detector cooled by liquid Nitrogen. Raman excitation at 1064 nm was provided by a Nd:YAG. The laser power measured at the sample was 100 mW, and spectra were accumulated for 50 scans at 4 cm^{-1} resolution in back scattering geometry.

RESULT AND DISCUSSION

1. IR and Raman spectra for CH_3 /$CD_3Co(DH)_2H_2O$

Fig.1a is the Raman spectra of $CH_3Co(DH)_2H_2O$ and $CD_3Co(DH)_2H_2O$ (1600-100 cm^{-1}), Fig.1b is the IR spectra of the two complexes (1600-100 cm^{-1}),

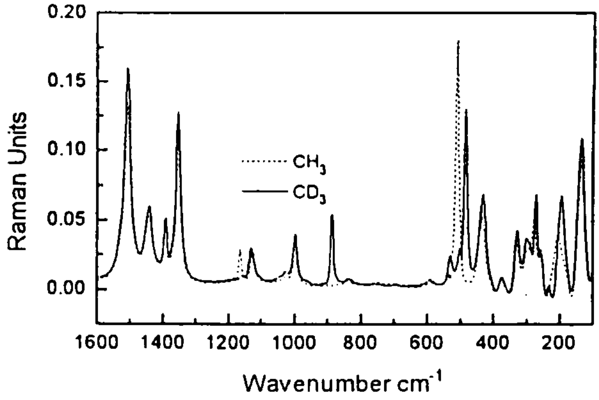

FIG.1a Raman spectra of $RCo(DH)_2H_2O$ ($R=CH_3$, CD_3)

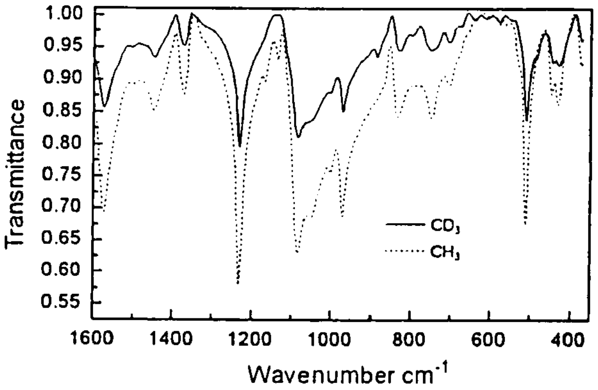

FIG.1b IR spectra of $RCo(DH)_2H_2O$ ($R=CH_3$, CD_3)

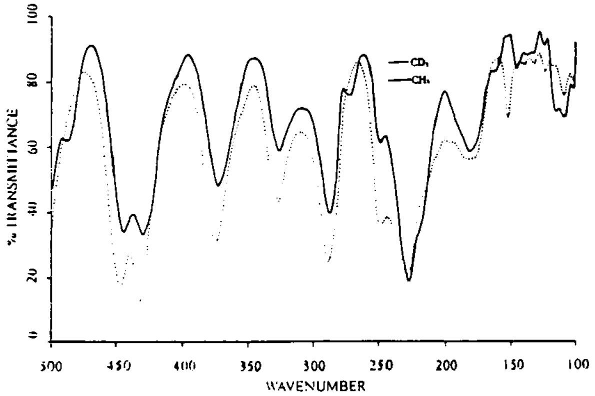

FIG.1c Far IR spectra of $RCo(DH)_2H_2O$ ($R=CH_3$, CD_3)

Fig.1c is the IR spectra of the two complexes (500-100 cm^{-1}). Table 1 lists the observed IR and Raman frequencies and empirical band assignments of the two complexes.[9,10]

In order to aid assignment of Co-C bond stretching vibrational frequency. The isotopic substitution $CD_3Co(DH)_2H_2O$ has been prepared, in which the H/D substitution at methyl group is expected to cause the shift of Co-C bond stretching vibrational frequency. Comparing the Raman Spectra of the two complexes, the strong band at 511 cm^{-1} of $CH_3Co(DH)_2H_2O$ can be assigned to Co-C stretching mode, which shift to 485 cm^{-1} in $CD_3Co(DH)_2H_2O$ (theoretical calculated shift is 475 cm^{-1} [11]). Comparing the IR spectra of the two complexes, besides the band at 511 cm^{-1} of $CD_3Co(DH)_2H_2O$, which is assigned to Co-N stretching mode by earlier studies,[6] there is a new weak shoulder band at 486 cm^{-1}, to which Co-C stretching contribute. Therefore, the strong band at 511 cm^{-1} of $CH_3Co(DH)_2H_2O$ is assigned to be a coupling band of Co-C with Co-N stretching modes. Since IR spectrum is absorbing spectrum and Raman spectrum is scattering spectrum, the band intensity of the two complexes is not completely same, even the strong-intensity Co-N band in IR spectra shows the weak-intensity band in Raman spectra. However, in earlier studies only one kind of spectra was used for analysis, the band assignment of Co-C stretching mode has been controversial.

2. Normal coordinate analysis

In the preceding section, we have assigned that the 511 cm^{-1} band is a coupling band of Co-N and Co-C stretching modes based on the observed isotopic shifts of the two spectra. In order to give definitive band assignment and to estimate theoretical isotopic shifts, we have carried out normal coordinate analysis on 26-atom CH_3 / $CD_3Co(DH)_2H_2O$ as shown in Fig. 2. Since our main interest is focused in Co-C and Co-N stretching vibrations, all the methyl hydrogen vibrations of dimethylglyoximate are neglected in our calculations. This approximation does not cause appreciable errors in our calculations because C-H frequencies are too high to couple with Co-C and Co-N stretching modes.[12]

TABLE 1: Vibrational Spectra of $RCo(DH)_2H_2O(R=CH_3, CD_3)$

$CH_3Co(DH)_2H_2O$		$CD_3Co(DH)_2H_2O$		
IR	Raman	Raman	IR	Assignment
3093.6			3091.3	asy Ow-H
3003.0	3005.0	3006.3	3007.0	sys Ow-H
	2955.1	2954.8	2970.0	
2922.6	2922.5	2922.5	2923.7	sys Cm-H
2901.4	2903.1			sys C-H
2792.0	2733.1	2729.4		
2317.0			2324.3	O-H
		2242.5	2239.3	asy C-D
		2110.2	2109.8	sys C-D
		2050.5	2050.5	C-D
			1726.5	OHO
1572.5			1572.3	C=N
1502.5	1508.3	1507.8	1504.2	dcf HCmH
1447.1	1441.3	1441.3	1447.0	HCmH
1372.3	1392.8	1392.8	1372.2	
	1354.2	1354.4		
1231.0			1231.0	N-O
1168.9	1165.2			HCH
1136.2	1126.2	1130.6		
1082.8			1083.1	N-O
1053.4			1058.5	
1001.5	997.7	998.2	1002.9	
971.9			971.5	HCmC
		886.9	886.9	DCD
834.3	837.4		830.1	
			797.2	
748.9			749.6	
705.4			704.3	
			676.9	
636.7			643.7	
611.6			611.4	
580.0	591.8	592.8	580.2	
561.0				
		531.0		
511.3	511.5	501.8	510.5	Co-C or Co-N
470.0		484.5	486.0	
447.3			444.9	
432.5	436.1	433.3	430.4	
374.5	376.5	374.7	373.1	Co-O
326.0	332.1	328.7	325.7	
288.9		299.2	287.6	
	276.2	271.0	271.4	
248.7	257.3		249.1	
228.3		232.5	228.4	
196.5	206.4	195.2		
182.5			181.4	
152.3			145.7	
139.1	134.2	134.8	137.4	
131.5				
123.3			123.6	
			115.4	
108.3			108.9	

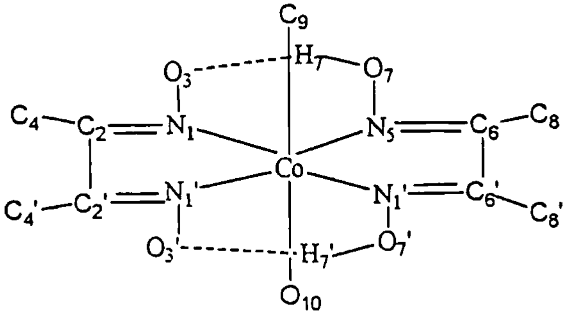

FIG.2 Molecular structure of $CH_3Co(DH)_2H_2O$

The structure parameters used in the normal coordinate analysis (NCA) were taken from Ref.[13]. The calculation was performed on a 486 PC using GMAT and FPERT programs provided by National Research Council of Canada.[14] 102 internal coordinates were used as shown in Fig. 3, 29 of which were attributed to stretching, 51 to bending and 22 to twisting. A Urey-Bradley force field was used in the calculation. The initial values of the force constants were transferred from related molecules[15,16,17,18] and refined in accordance with the position of the bands in the IR and Raman spectra. The final values of force constants are collected in Table 2. The observed and the calculated frequencies together with percentages of potential energy distribution (PED) for two complexes are presented in Table 3-4. The calculated frequencies agree well with the observed ones.

From the Table 3-4, the PED characterizes the frequencies calculated at 2322.2 cm^{-1} as antisymmetric stretching vibration of two asymmetrical O-H bonds and at 1725.7, 1725.1 cm^{-1} as OHO bending vibration, the intensity of two vibrations is very wear and is not easy observed in spectra. The PED shows the frequencies calculated at 1572.6 and 1568.6 cm^{-1} as antisymmetrical stretching modes of the C=N bonds, correspond to the band observed at 1572.5 cm^{-1}. The calculated frequencies at 1547.9 and 1540.2 cm^{-1} are stretching vibration of C=N bond and C-C bond.

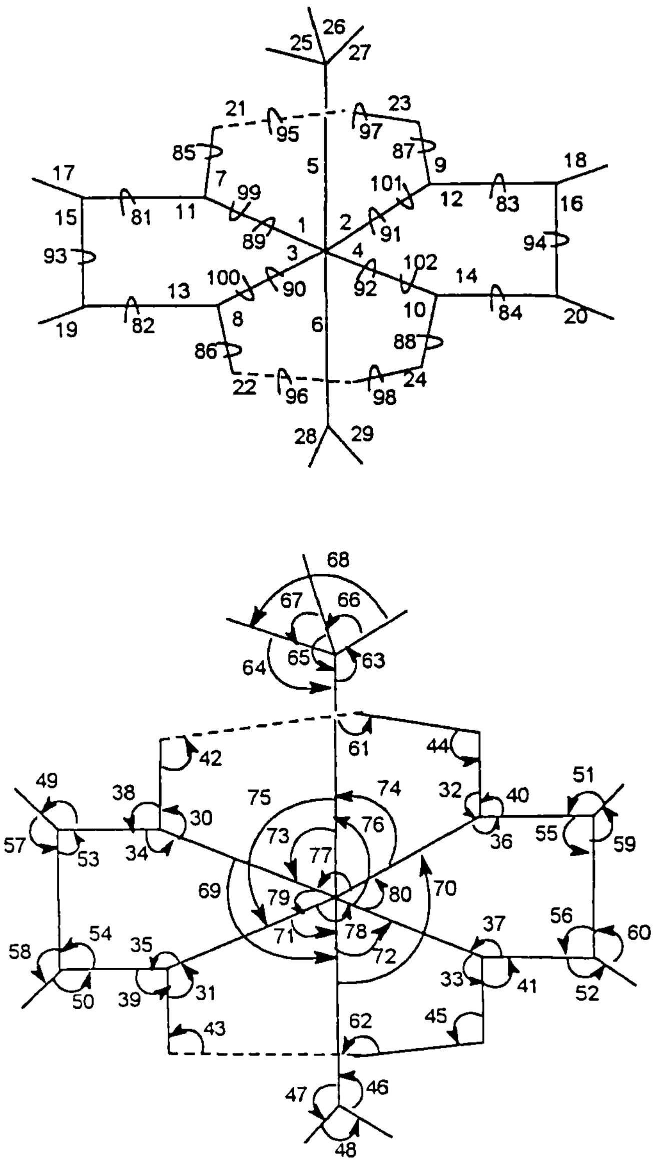

FIG.3 Numerical identification of internal coordinates for $CH_3Co(DH)_2H_2O$

TABLE 2: The Force Constants for $RCo(DH)_2H_2O(R=CH_3, CD_3)$#

symbol	coordinates involved	value	symbol	coordinates involved	value
K_1	$Co\text{-}N_1$	1.9435	H_{31}	N_1CoN_1'	0.1500
K_2	$Co\text{-}C_9$	1.0493	T_{32}	$CoN_1C_2C_2'$	0.0015
K_3	$Co\text{-}O_{10}$	0.8595	T_{33}	$CoN_1O_3H_7$	0.0015
K_4	$N1\text{-}O_3$	4.8505	T_{34}	$CoN_5O_7H_7$	0.0012
K_5	$N_5\text{-}O_7$	4.4405	T_{35}	$C_2N_1CoN_1'$	0.0014
K_6	$N1=C_2$	6.8035	T_{36}	$N_1C_2C_2'N_1'$	0.0025
K_7	$C_2\text{-}C_2'$	4.8388	T_{37}	$N_1O_3H_7O_7$	0.0001
K_8	$C_2\text{-}C_4$	2.6532	T_{38}	$N_5O_7H_7O_3$	0.0001
K_9	$O_3\text{-}H_7$	1.3356	T_{39}	$O_3N_1CoN_5$	0.0020
K_{10}	$O_7\text{-}H_7$	1.6806	T_{40}	$O_7N_5CoN_1$	0.0030
K_{11}	$C_9\text{-}H_{91}$	4.4976	F_{41}	CoN_1O_3	0.0020
K_{12}	$O_{10}\text{-}H_{10}$	4.9302	F_{42}	CoN_5O_7	0.0020
H_{13}	CoN_1O_3	0.5350	F_{43}	CoN_1C_2	0.0020
H_{14}	CoN_5O_7	0.5350	F_{44}	$O_3N_1C_2$	0.0500
H_{15}	CoN_1C_2	0.5347	F_{45}	$O_7N_5C_6$	0.0500
H_{16}	$O_3N_1C_2$	0.4440	F_{46}	$N_1O_3H_7$	0.1030
H_{17}	$O_7N_5C_6$	0.4440	F_{47}	$N_5O_7H_7$	0.1030
H_{18}	$N_1O_3H_7$	0.2850	F_{48}	$CoO_{10}H_{10}$	0.0695
H_{19}	$N_5O_7H_7$	0.2950	F_{49}	$H_{10}O_{10}H_{10}'$	0.3793
H_{20}	$CoO_{10}H_{10}$	0.2245	F_{50}	$N_1C_2C_4$	0.7510
H_{21}	$H_{10}O_{10}H_{10}'$	0.3328	F_{51}	$N_1C_2C_2'$	0.3580
H_{22}	$N_1C_2C_4$	0.5506	F_{52}	$C_4C_2C_2'$	0.7410
H_{23}	$N_1C_2C_2'$	0.8040	F_{53}	$O_3H_7O_7$	0.1015
H_{24}	$C_4C_2C_2'$	0.4840	F_{54}	CoC_9H_{91}	0.1755
H_{25}	$O_3H_7O_7$	0.4555	F_{55}	$H_{91}C_9H_{92}$	0.0555
H_{26}	CoC_9H_{91}	0.1745	F_{56}	$O_{10}CoN_1$	0.1750
H_{27}	$H_{91}C_9H_{92}$	0.2143	F_{57}	C_9CoN_1	0.1750
H_{28}	$O_{10}CoN_1$	0.2850	F_{58}	N_1CoN_5	0.0300
H_{29}	C_9CoN_1	0.4780	F_{59}	N_1CoN_1'	0.0300
H_{30}	N_1CoN_5	0.2900			

#Notation and dimension are as follows: K—strecting force constant (mdyn · $Å^{-1}$); H—bending force constant (mdyn · Å); F—repulsive force constant (mdyn · $Å^{-1}$); T—twisting force constant (mdyn · $Å^{-1}$).

TABLE 3: Calculated and Observed Frequency and Percent PED for $CH_3Co(DH)_2H_2O$

Raman (cm^{-1})	IR (cm^{-1})	Calc.	potential energy distribution (%)
	3093.6	3091.6	90.1K12+9.5F49
3005.0	3003.0	3004.1	100.0K12
2955.1		2958.8	98.2K11
2922.5	2922.6		
2903.1	2901.4	2901.3	97.6K11
2733.1	2792.0	2847.3	96.1K11
	2317.0	2322.2	57.8K10+39.2K9
		2322.2	57.8K10+39.2K9
		1725.7	67.9H25+13.5H19
		1725.1	68.4H25+13.5H19
		1627.7	67.2H21+12.4H20+17.4F49
	1572.5	1572.6	67.4K6
		1568.6	67.6K6
		1547.9	60.9K6+19.7K7
		1540.2	61.7K6+19.7K7
1508.3	1502.5		
1441.3	1447.1		
1392.8	1372.3		
1354.2		1351.4	35.6K7+30.9K8+13.8K6
		1349.0	35.3K7+31.0K8+13.8K6
		1255.8	60.7H27+24.3H26+9.9F54
	1231.0	1230.3	32.4K4+22.5K8+12.5H23
		1221.8	32.9K5+22.0K8+11.9H23
1165.2	1168.9	1168.7	85.6H27+9.5F55
1126.2	1136.2		
	1082.8	1084.2	36.5K4+31.7K5+10.6K1
	1053.4	1070.9	36.4K5+31.8K4
		1026.5	67.6K27+16.3K26
997.7	1001.5	1000.8	35.7K8+23.8K5+9.2F50
	971.9	995.2	35.8K8+22.9K4+10.2K1+9.2F50
		917.2	42.6K8+17.7F50+10.7F52
		912.7	43.1K8+18.6F50+10.5F52
837.4	834.3	834.6	86.1H20+13.0F48
		784.5	58.1H26+32.4F54
		773.7	10.5K1+12.5H22+12.9H24+11.3F50+12.9F52

(continued)

TABLE 3: (Continued)

Raman (cm^{-1})	IR (cm^{-1})	Calc.	potential energy distribution (%)
	748.9	753.9	9.7K1+14.2H22+14.7H24+13.8F50+14.6F52
	705.4	707.7	50.8H26+13.3H27+30.5F54
	636.7	644.4	73.8H20+10.9H21
	611.6		
591.8	580.0		
	561.0	537.1	21.3K9+14.5K10
		535.1	23.7H23+9.7K52
		527.2	20.2H23
511.5	511.3	512.0	22.0K1+28.3K2+11.4F54
		509.2	24.5K1+26.0K2+11.1F54
	470.0	499.3	23.2K9+16.0K10
	447.3	442.8	10.9H19+17.2T37+17.2T38
436.1	432.5	428.3	20.3T37+20.3T38
		413.3	10.7K1+13.3K9
		412.0	46.5K1+10.5F50
376.5	374.5	374.5	54.2K3+13.4F56
		366.8	14.4H15+11.1H22+12.0F50
		340.9	18.7H24+22.2F52
332.1	326.0	324.1	22.0H24+21.2F52
		309.8	20.6K1+10.4H22+14.1F50
		308.4	36.5H29+26.8F57
	288.9	289.5	18.0H28+27.3H29+22.7F56+19.0F57
		289.2	13.6H28+36.4H29+16.9F56+28.7F57
		285.7	14.2H28+14.8F56
276.2		276.6	36.8K1+12.8H18
257.3	248.7	251.6	16.0K1+11.9HH14+16.0H15
	228.3	228.0	18.4H28+31.0H29+23.8F56+23.9F57
206.4		204.9	19.6H28+10.5H29+26.4F56
	196.5	195.4	23.0H28+12.5H29+33.4F56+11.4F57
	182.5		
	152.3	147.5	9.2H28+12.2F56
	139.1		
134.2	131.5		
	123.3		
	108.3		

TABLE 4: Calculated and Observed Frequency and Percent PED for $CD_3Co(DH)_2H_2O$

Raman (cm^{-1})	IR (cm^{-1})	Calc.	potential energy distribution (%)
	3091.3	3091.6	90.1K12+9.5F49
3006.3	3007.0	3004.1	100.0K12
2954.8	2970.0		
2922.5	2923.7		
2729.4			
	2324.3	2322.2	57.8K10+39.2K9
		2322.2	57.8K10+39.2K9
2242.5	2239.3	2217.7	97.9K11
2110.2	2109.8	2134.6	97.6K11
2050.5	2050.5	2043.7	95.7 K11
	1726.5	1725.7	67.9H25+13.5H19
		1725.1	68.4H25+13.5H19
		1627.7	67.2H21+12.4H20+17.4F50
	1572.3	1572.6	67.4K6
		1568.6	67.6K6
		1547.9	60.9K6+19.7K7
		1540.2	61.7K6+19.7K7
1507.8	1504.2		
1441.3	1447.0		
1392.8	1372.2		
1354.4		1351.4	35.6K7+30.9K8+13.8K6
		1349.0	35.3K7+31.0K8+13.8K6
	1231.0	1230.2	32.4K4+22.6K8+12.5H23
		1221.8	32.9K5+22.0K8+11.9H23
1130.6			
	1083.1	1084.1	36.8K4+31.4K5+10.6K1
	1058.5	1071.0	36.8K5+31.4K4
998.2	1002.9	1000.8	35.7K8+23.8K5
	971.5	995.2	35.8K8+23.0K4+10.2K1
		949.6	56.4H27+25.4H26
		917.2	42.6K8+17.7F50+10.7F52
		912.5	42.8K8+18.5F50+10.4F52
886.9	886.9		
	830.1	838.2	86.8H27
		834.5	85.9H20+13.0F48

(continued)

TABLE 4: (Continued)

Raman (cm^{-1})	IR (cm^{-1})	Calc.	potential energy distribution (%)
	797.2	774.0	11.2K1+12.8H22+13.2H24+11.5F50+13.2F52
	749.6	753.9	9.7K1+14.2H22+14.7H24+13.3F50+14.6F52
		751.9	74.3H27+10.7H26
	704.3		
	676.9		
	643.7	644.5	73.8H20+10.9H21
592.8	611.4	590.5	58.7H26+33.1F54
	580.2		
		552.7	44.3H26+26.5F54
		536.8	21.6K9+14.7K10
531.0		535.1	23.7H22
		526.9	20.4H22
	510.5	505.5	39.1K1
501.8		499.1	23.3K9+16.0K10
484.5	486.0	478.5	45.0K2+12.4K3+24.7F54
	444.9	442.8	10.9H19+17.2T37+17.2T38
433.3	430.4	428.0	20.6T37+20.6T38
		413.0	11.0K1+13.5K9
		409.8	47.5K1+10.5F50
374.7	373.1	368.5	47.7K3+14.0F56
		365.1	14.0H15+10.4H22+11.5F50
		340.4	19.9H24+23.5F52
328.7	325.7	323.8	21.9H24+21.0F52
		309.7	20.7K1+105H22+14.2F50
299.2		292.4	27.2H29+18.0F57
	287.6	287.8	18.0H28+24.3H29+21.6F56+18.4F57
		284.6	19.3H28+12.1H29+21.3F56+10.4F57
		279.1	16.4H28+29.4H29+20.9F56+23.0F57
271.0	271.4	276.5	35.2K1+12.0H18
	249.1	251.5	16.0K1+11.9H14+16.0H15
232.5	228.4	228.0	18.4H28+31.0H29+23.7F56+23.9F57
195.2		199.7	14.9H28+12.4H29+20.2F56+9.9F57
	181.4	186.7	20.2H28+16.9H29+29.1F56+14.9F57
	145.7	144.1	10.2H28+13.5F56
134.8	137.4		
	123.6		
	115.4		
	108.9		

From the PED several frequencies show a N-O stretching character: the frequencies calculated at 1084.2 and 1070.9 cm^{-1} are coupling modes in which the two N-O bonds belonging to two DH molecules, respectively. The corresponding observed band is at 1082.8 cm^{-1}. For the other frequencies calculated at 1230.3 and 1221.8 cm^{-1} which have some N-O stretching character with considerable mixing of other vibrational modes, correspond to the band observed at 1231.0 cm^{-1}. The results of the present normal coordinate analysis support the some empirical assignment,[4,5,6,9,10] and only minor difference from that of Bigotto ($Co(DH)_2$),[15] probably due to the slightly changes of the structural parameters in calculation.

As for the NCA of the vibrational mode around the cobalt, which have not reported, our result revealed that the frequencies calculated at 1255.8, 1168.7, 1026.5 cm^{-1} are bending vibration of axial methyl group, the middle frequency corresponds to the band observed at 1168.7 cm^{-1}. The frequencies calculated at 784.5 and 707.7 cm^{-1} are CoCH vibration, the second frequency corresponds to the band observed at 707.7 cm^{-1}. Besides, the frequencies calculated at 834.6 and 644.4 cm^{-1} are rocking and wagging vibrations in H_2O,[19] respectively, correspond to the bands observed at 834.3 and 636.7 cm^{-1}.

It is interesting to note that several vibrations below 600 cm^{-1} are more or less coupled with the metal-nitrogen stretching mode. The PED characterizes the frequency calculated at 512.0 and 509.2 cm^{-1} as Co-N and Co-C bond coupling modes, correspond to the band observed at 511.3 cm^{-1}. The frequency calculated at 374.5cm^{-1} is Co-C stetching modes with some OCoN, corresponds to the band observed at 374.5 cm^{-1}. In a normal coordinate analyses of isotopic substitution $CD_3Co(DH)_2H_2O$, the calculated frequency of Co-C moves to 478.5 cm^{-1}, which agrees quite closely with the theoretical calculated shift value 475 cm^{-1} [11] and corresponds to the band observed at 486.0 cm^{-1}. The frequencies calculated at 412.0, 309.8 and 276.6 cm^{-1} have a remarkable Co-N stretching character, although they are not pure vibrations.

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