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Normal coordinate analysis and spectral band assignments for the in-plane infrared active vibrations of diaquo tetra-μ-acetato dichromium (II) complex

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ABSTRACT

The 29 in-plane infrared active normal modes of diaquo tetra-μ-acetato dichromium (II) complex have been described and their frequencies of vibration calculated by normal coordinate analysis. On the basis of these calculations, 25 bands in the infrared spectrum of the complex have been assigned to the in-plane modes. The remaining 4 bands were predicted to fall out of the range of our investigation. However, 6 accidental degeneracies were identified thus reducing the total number of assigned bands to actually be 19. Furthermore, the values of the forces constants of COO and bridging Cr-O bonds in $Cr_2(O_2CCH_3)_4(H_2O)_2$ complex and $Cr_2(O_2CH)_4(H_2O)_2$ previously reported suggest that the strengths of these bonds are inversely related.

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INTRODUCTION

Because of the importance of assigning M-M and symmetric bridging M-O stretching frequencies in the study of the electronic absorption spectra of $M_2(O_2CR)_4L_2$ complexes, the vibrational spectra of some of these complexes have been studied [1-8]. However, it has recently been shown [9] that all previous infrared spectral investigations on tetra-μ-acetato dichromium (II) adducts, $Cr_2(O_2CCH_3)_4L_2$, were only concerned with CH_3COO^- and L vibrations [10, 11], and that no information is as yet available on its Cr-Cr and bridging Cr-O vibrations. Thus there is the need to obtain the vibrational spectra of the tetra-μ-acetato dichromium (II) complexes and theoretically assign the bands, especially the Cr-Cr and bridging Cr-O stretching bands. Such studies will also furnish information about the extent of mixing between these vibrations and other internal coordinates as well as provide data which will permit more precise assignments of their electronic absorption bands. In addition, studies of the vibrational spectra of the tetra-μ-acetato dichromium (II) complexes themselves are interesting from the viewpoint of molecular spectroscopy since thus far no normal coordinate treatments have been made on such bridging ring systems, where coupling between vibrational modes may occur and the concept of *group frequency* may be broken down.

In order to achieve the purpose mentioned above, we have obtained the infrared spectrum of diaquo tetra-μ-acetatodichromium(II) complex, $Cr_2(O_2CCH_3)_4(H_2O)_2$, and made normal coordinate analyses on it. Because of the large size of this complex, however, the report of the analyses is in three parts. In a previous paper [9], the results of the calculations of all the 102 genuine internal coordinates of the complex, the assignments of these to vibrational modes, the identification of their activity in infrared or Raman and their classification with respect to type as well as whether in-plane or out-of-plane was presented. In this article, the results of the normal coordinate analysis of the infrared active in-plane normal vibrations of the complex are reported and discussed.

EXPERIMENTAL

(a) Preparation of Complex and Spectral Measurements

Diaquo tetra-μ-acetato dichromium (II) complex, $Cr_2(O_2CCH_3)_4(H_2O)_2$, was prepared according to a standard method described in the literature [12]. However, the infrared spectrum was obtained, using a Matson Genesis FT-IR Spectrophotometer, in the range 4000 - 400 cm^{-1}. The nujol mull method was employed for the preparation of the sample. The absorption curve and some of the observed frequencies are shown in Fig. 1 and Table 1, respectively.

Table 1: Comparison of observed and calculated frequencies of $Cr_2(O_2CCH_3)_4(H_2O)_2$ complex (cm^{-1})

		Obs. Freq.	Calc. Freq.	Potential energy distribution*	Assignment
1.	υ_{74}	2853.42s	2853.50	$S_{74}(99.99)$	$\upsilon_s''(CH_3)$
2.	υ_{75}	2953.65s	2952.32	$S_{75}(99.98)$	$\upsilon_s'''(CH_3)$
3.	υ_{76}	933.50w	932.66	$S_{76}(68.57)$, $S_{77}(31.42)$	$\upsilon_s'(C\text{-}C) + \upsilon_s'(COO)$
4.	υ_{77}	1454.92s	1454.81	$S_{76}(3.58)$, $S_{77}(96.40)$	$\upsilon_s'(COO) + \upsilon_s'(C\text{-}C)$
5.	υ_{78}	623.15m	622.10	$S_{78}(45.88)$, $S_{84}(53.89)$	$\upsilon_s'(OCrO)$
6.	υ_{79}	3358.17m	3358.32	$S_{79}(99.99)$	$\upsilon_s'(H_2O)$
7.	υ_{80}	2866.62s,sh	2888.06	$S_{80}(99.99)$	$\upsilon_s''(CH_3)$
8.	υ_{81}	2925.08vs	2925.14	$S_{81}(99.99)$	$\upsilon_s'''(CH_3)$
9.	υ_{82}	933.50w	932.68	$S_{82}(68.56)$, $S_{83}(31.42)$	$\upsilon_s'(C\text{-}C) + \upsilon_s'(COO)$
10.	υ_{83}	1454.92s	1454.80	$S_{82}(3.58)$, $S_{83}(96.40)$	$\upsilon_s'(COO) + \upsilon_s'(C\text{-}C)$
11.	υ_{84}	623.15m	622.39	$S_{78}(53.90)$, $S_{84}(45.83)$	$\upsilon_s'(OCrO)$
12.	υ_{85}	1378.22s	1378.88	$S_{85}(99.93)$	$\delta_s''(CH_3)$
13.	υ_{86}	1522.51s	1522.95	$S_{86}(99.40)$	$\delta_s'''(CH_3)$
14.	υ_{87}	795.57w	795.60	$S_{87}(96.69)$, $S_{92}(1.40)$	$\delta_s'(Ring)$
15.	υ_{88}	879.31w	879.83	$S_{79}(1.16)$, $S_{88}(93.99)$, $S_{99}(3.24)$	$r_s(H_2O) + r_s'(H_2O) + \upsilon_s'(H_2O)$
16.	υ_{89}	965.52w	964.56	$S_{76}(3.56)$, $S_{77}(1.77)$, $S_{89}(92.48)$	$r_s'(CH_3) + \upsilon_s'(C\text{-}C) + \upsilon_s'(COO)$
17.	υ_{90}	1559.45s	1561.89	$S_{90}(98.56)$, $S_{91}(1.27)$	$\delta_s''(CH_3) + \delta_s'''(CH_3)$
18.	υ_{91}	1485.84s	1486.39	$S_{91}(94.94)$, $S_{90}(4.33)$	$\delta_s'''(CH_3) + \delta_s''(CH_3)$
19.	υ_{92}	722.05m	723.57	$S_{84}(1.01)$, $S_{87}(1.10)$, $S_{92}(82.78)$, $S_{100}(1.08)$, $S_{101}(13.07)$	$\delta_s'(Ring) + r_s'(COO) + r_s'(C\text{-}C) + \upsilon_s'(OCrO)$
20.	υ_{93}	965.52w	966.23	$S_{82}(3.41)$, $S_{83}(1.69)$, $S_{93}(92.83)$	$r_s'(CH_3) + \upsilon_s'(C\text{-}C) + \upsilon_s'(COO)$
21.	υ_{94}	475.93w	475.27	$S_{94}(64.92)$, $S_{100}(33.73)$	$r_s'(C\text{-}C)$
22.	υ_{95}	675.59s	678.79	$S_{95}(98.54)$	$r_s'(COO)$
23.	υ_{96}	-	104.46	$S_{96}(50.04)$, $S_{102}(49.93)$	$\delta_s(OCrO)$
24.	υ_{97}	-	34.82	$S_{78}(7.16)$, $S_{84}(7.37)$, $S_{87}(1.66)$, $S_{92}(2.67)$, $S_{96}(4.06)$, $S_{97}(69.36)$,$S_{98}(3.24)$,$S_{102}(4.48)$	$\pi(Cr\,–Cr) + \upsilon_s'(OCrO) + \delta_s(OCrO) + r_s(Cr\text{-}O) + \delta_s'(Ring)$
25.	υ_{98}	-	56.47	$S_{97}(5.84)$, $S_{98}(90.50)$	$r_s\ (Cr\ \text{-}O) + \pi(Cr\,–Cr)$
26.	υ_{99}	1155.65w	1156.51	$S_{99}(99.87)$	$r_s'(H_2O)$
27.	υ_{100}	475.93w	475.59	$S_{94}(34.02)$, $S_{100}(65.24)$	$r_s'(C\ \text{-}\ C)$
28.	υ_{101}	675.59s	675.32	$S_{92}(5.50)$, $S_{101}(92.83)$	$r_s'(COO) + \delta_s'(Ring)$
29.	υ_{102}	-	90.18	$S_{87}(1.91)$, $S_{92}(2.29)$, $S_{96}(42.21)$, $S_{97}(10.17)$, $S_{98}(42.06)$	$\delta_s(OCrO) + r_s\ (Cr\ \text{-}O) + \pi(Cr\,–Cr) + \delta_s'(Ring)$

Band relative intensities: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

* The meaning of the internal coordinates, S_i, i = 74 – 102, see ref. 9.

(b) Calculations

As previously reported [9], the diaquo tetra-μ-acetatodichromium(II) complex has 28$\mathbf{A_g}$ + 29$\mathbf{B_u}$ in-plane normal vibrations. The internal coordinates representing these vibrations were also given there. Furthermore, it was identified that only those normal vibrations that belong to the $\mathbf{B_u}$ class are active in the infrared. Thus only the 29$\mathbf{B_u}$ normal modes need be considered for normal coordinate treatment of the in-plane vibrations of the complex in the infrared spectral investigation.

The elements of the **G** matrix for the $\mathbf{B_u}$ class of normal vibrations of the complex were calculated using the Wilson's method [13] and transferable valence force field was adopted for constructing the **F** matrix. However, the conventions of Hollenstein and co-workers [14] were followed in setting up the **F** matrix. The application of those criteria left 45 distinct force constants for the $\mathbf{B_u}$ type vibrations of the complex. Initial force constants for groups in the complex were taken from the force fields of diaquo tetra-μ-formato dichromium (II) complex [15] and the acetate ion [16]. Then, matrix secular equations of the form, $|\mathbf{GF} - E\Lambda| = 0$, were solved. After several iterations, a satisfactory set of force constants, listed in Table 2, was obtained. In Table 1, the frequencies calculated from this set of force constants are compared with the values observed for the complex. Agreement between the calculated and observed values is good. The potential energy distribution in each normal mode was calculated with respect to each internal coordinate in order to make theoretical band assignments and to determine the mixing ratio of various normal modes in each band.

Table 2: Force constants (x 10^5 dyne cm^{-1}) of the $Cr_2(O_2CH_3)_4(H_2O)_2$

A. Diagonal Force constants				B.	Interaction force constants cont'd		
	Coordinate		Value		Coordinates		Value
1.	$\upsilon_s''(CH_3)$		4.706246	35.	$\upsilon_s'(OCrO)$	$\upsilon_s'(OCrO)$	0.000421
2.	$\upsilon_s'''(CH_3)$		4.653835	36.		$\delta_s'(Ring)$	0.033524
3.	$\upsilon_s'(C–C)$		3.593242	37.		$r_s'(COO)$	0.056359
4.	$\upsilon_s'(COO)$		12.615834	38.		$\delta_s(OCrO)$	0.045341
5.	$\upsilon_s'(OCrO)$		2.260990	39.		$\pi(Cr-Cr)$	0.084632
6.	$\upsilon_s'(H_2O)$		6..300052	40.	$\upsilon_s'(OCrO)$	$r_s(Cr-O)$	0.055411
7.	$\delta_s''(CH_3)$		0.935128	41.	$\upsilon_s'(H_2O)$	$r_s(H_2O)$	0.057364
8.	$\delta_s'''(CH_3)$		0.502247	42.		$r_s(Cr-O)$	0.001103
9.	$\delta_s'(Ring)$		0.725045	43.		$r_s'(H_2O)$	0.005910
10.	$r_s(H_2O)$		0.049623	44.	$\upsilon_s'(COO)$	$\upsilon_s'(OCrO)$	0.002490
11.	$r_s'(CH_3)$		0.244875	45.		$\delta_s'(Ring)$	0.003716
12.	$r_s'(C-C)$		0.825268	46.		$r_s'(C-C)$	0.123270
13.	$r_s'(COO)$		1.174164	47.		$r_s'(COO)$	0.143136
14.	$\delta_s(OCrO)$		0.061748	48.		$\delta_s'(OCrO)$	0.007261
15.	$\pi(Cr-Cr)$		0.058624	49.	$\delta_s''(CH_3)$	$r_s(CH_3)$	0.020209
16.	$r_s(Cr-O)$		0.042876	50.		$r_s'(C-C)$	0.011561
17.	$r_s'(H_2O)$		0.704346	51.	$\delta_s'''(CH_3)$	$r_s'(CH_3)$	0.004260
				52.		$r_s'(C-C)$	0.010120
B.	**Interaction force constants**			53.	$\delta_s'(Ring)$	$\delta_s'(Ring)$	-0.014065
	Coordinates		Value	54.		$r_s'(C-C)$	0.040551
18.	$\upsilon_s''(CH_3)$	$\upsilon_s'(C-C)$	0.003521	55.		$\delta_s(OCrO)$	0.030110
19.		$\delta_s''(CH_3)$	0.002652	56.		$r_s'(COO)$	0.017172
20.		$\delta_s'''(CH_3)$	0.002017	57.		$\pi(Cr-Cr)$	0.025844
21.		$r_s'(CH_3)$	0.010365	58.		$r_s(Cr-O)$	0.019461
22.		$r_s'(C-C)$	0.008518	59.	$r_s(H_2O)$	$r_s\ (Cr-O)$	0.002375
23.	$\upsilon_s'''(CH_3)$	$\upsilon_s'(C-C)$	0.014262	60.		$r_s'(H_2O)$	0.250067
24.		$\delta_s''(CH_3)$	0.010173	61.	$r_s'(CH_3)$	$r_s'(C-C)$	0.008366
25.		$\delta_s'''(CH_3)$	0.020051	62.	$r_s'(C-C)$	$r_s'(COO)$	0.027015
26.		$r_s'(CH_3)$	0.000507	63.	$r_s'(COO)$	$\delta_s(OCrO)$	0.004588
27.		$r_s'(C-C)$	0.006251	64.	$\delta_s(OCrO)$	$\pi(Cr-Cr)$	0.001091
28.	$\upsilon_s'(C-C)$	$\upsilon_s'(COO)$	1.407364	65.		$r_s(Cr-O)$	0.006457
29.		$\delta_s''(CH_3)$	0.060241	66.		$\delta_s(OCrO)$	0.000874
30.		$\delta_s'''(CH_3)$	0.133275	67.	$\pi\ (Cr-Cr)$	$r_s(Cr-O)$	0.005133
31.		$\delta_s'(Ring)$	0.002491	68.	$r_s(Cr-O)$	$r_s'\ (H_2O)$	0.004220
32.	$\upsilon_s'(C-C)$	$r_s'(CH_3)$	0.018370				
33.		$r_s'(C-C)$	0.035498				
34.		$r_s'(COO)$	0.024725				

RESULTS AND DISCUSSION

Some of the frequencies of diaquo tetra-μ-acetato dichromium (II) infrared absorptions, which were assigned to its $\mathbf{B_u}$ vibrations, are listed in Table 1. But the structure of the 29$\mathbf{B_u}$ in-plane normal vibrations of the complex was shown to be made up of 10$\mathbf{B_u}$ CH_3 + 4$\mathbf{B_u}$ C-C + 4$\mathbf{B_u}$ COO + 4$\mathbf{B_u}$ OCrO + 1$\mathbf{B_u}$ Cr-Cr + 1$\mathbf{B_u}$ Cr-O + 3$\mathbf{B_u}$ H_2O + 2$\mathbf{B_u}$ Ring motions. For example, the 10$\mathbf{B_u}$ CH_3 in-plane normal vibrations were assigned to the 2925, 2866, 2853, 1560, 1523, 1486, 1378 and 966 cm^{-1} bands. However, the bands at 2853 and 966 cm^{-1} represent frequencies of doubly degenerate vibrations each. Furthermore, the motions describing the bands at 1560, 1486 and 966 cm^{-1} are mixed vibrations. Also, the 4$\mathbf{B_u}$ C-C vibrations are described by only two bands. These are located at 934 and 476 cm^{-1}; both represent frequencies of doubly degenerate vibrations.

The 4$\mathbf{B_u}$ COO vibrations were assigned to 1455 and 676 cm^{-1} bands. The 1455 cm^{-1} band is due mainly to $\upsilon_s'(COO)$ with some little contribution from $\upsilon_s'(C-C)$ mode (~ 4%) and is doubly degenerate. The 676cm^{-1} band is similarly due to doubly degenerate vibrations. These are $r_s'(COO)$ and $r_s'(COO)$ coupled with $\delta_s'(Ring)$ mode. The 4$\mathbf{B_u}$ OCrO vibrations are made up of two stretching and linear bending motions each. Bands for

Table 3: Comparison of the frequencies (cm^{-1}) of some normal modes in $Cr_2(O_2CCH_3)_4(H_2O)_2$ and other compounds

Normal mode		$Cr_2(O_2CCH)_4(H_2O)_2$[a]	Cr(acac)$_2$[b]	$Cr_2(O_2CCH_3)_4(H_2O)_2$
1.	sym. C-H str.	2855		2853
2.	sym. C-H def.	1378	1370	1378
3.	sym. C-H rock	1010	1025	966
4.	sym. COO str.	1462		1455
5.	bridging sym. Cr-O str.	640		623
6.	sym. C-C str.		934	934
7.	sym. H_2O str.	3375		3358
8.	sym. H_2O rock	1174, 876		1156, 879
9.	sym. Ring def.	766, 722		796,722

a – ref. 9, and b – ref. 17.

Table 4: Force constants (x10^5dyne cm^{-1}) for some groups in the $Cr_2(O_2CCH_3)_4(H_2O)_2$ complex compared with values known for closer molecules/fragments

Cordinate(s)	Values		
	$Cr_2(O_2CH)_4(H_2O)_2$[a]	CH_3COO^{-}[b]	$Cr_2(O_2CCH_3)_4(H_2O)_2$
1. υ_s'' (CH_3)	4.464296	5.116283	4.706246
2. υ_s'''(CH_3)		4.848564	4.653835
3. υ_s'(COO)	10.956020	11.968535	12.614834
4. υ_s'(C-C)		3.024173	3.593242
5. υ_s'(OCrO)	2.747360		2.260990
6. υ_s'(H_2O)	6.336049		6.300052
7. δ_s''(CH_3)		1.104269	0.935128
8. δ_s'''(CH_3)		0.449008	0.502247
9. δ_s'(ring)	0.620866		0.725045
10. r_s'(CH_3)		0.279014	0.244875
11. r_s'(COO)		1.427166	1.174164
12. δ_s(OCrO)	0.062005		0.061748
13. r_s(H_2O)	0.021278		0.042876
14. r_s(Cr-O)	0.041765		0.0428876
15. υ_s'(COO) δ_s'(ring)	0.003647		0.003716
16. υ_s'(OCrO) δ_s'(ring)	0.072235		0.033524

[a] – ref. 9; and [b] – ref. 18.

the linear bending modes were predicted to be < 400 cm^{-1} and have not been observed because this falls below the lower limit of our investigation. The former modes were found to be doubly degenerate and assignable to the band at 623 cm^{-1}. Bands for Cr-Cr and axial Cr-O vibrations belonging to the $\mathbf{B_u}$ class have not been observed; the calculations indicated their frequencies to be less than 400 cm^{-1}.

The positions of the bands describing the 3$\mathbf{B_u}$ H_2O vibrations are located at 3358, 1156 and 879 ccm^{-1}, and are due to, υ_s'(H_2O), r_s'(H_2O) and r_s(H_2O) coupled with r_s'(H_2O) and υ_s'(H_2O) modes. The scissoring motions of the COO groups of the four bridging CH_3COO^- ligands is what effectively lead to the 2$\mathbf{B_u}$ Ring deformations. The study showed that the bands located at 796 and 722 cm^{-1} are assignable to these vibrations. They are, respectively, due to δ_s'(Ring) and δ_s'(Ring) coupled with r_s'(COO), r_s'(C-C) and υ_s'(OCrO) modes.

Of the many bands due to the in-plane vibrations of the complex, the Cr-Cr and bridging Cr-O symmetric stretching bands are of particular interest since both are useful in the study of the electronic absorption spectra of the complex. Unfortunately, Cr-Cr stretching mode belongs to the totally symmetric representation ($\mathbf{A_g}$) and is not active in the infrared. On the other hand, the bridging Cr-O bonds have symmetric stretching modes belonging to both $\mathbf{A_g}$ and $\mathbf{B_u}$ classes. The ones belonging to the $\mathbf{B_u}$ class have been observed and presented above. In Table 3 the frequencies of some normal modes in diaquo tetra-μ-acetato dichromium (II) and other molecules are compared. It is clear from the table that the frequencies of the eleven vibrations of

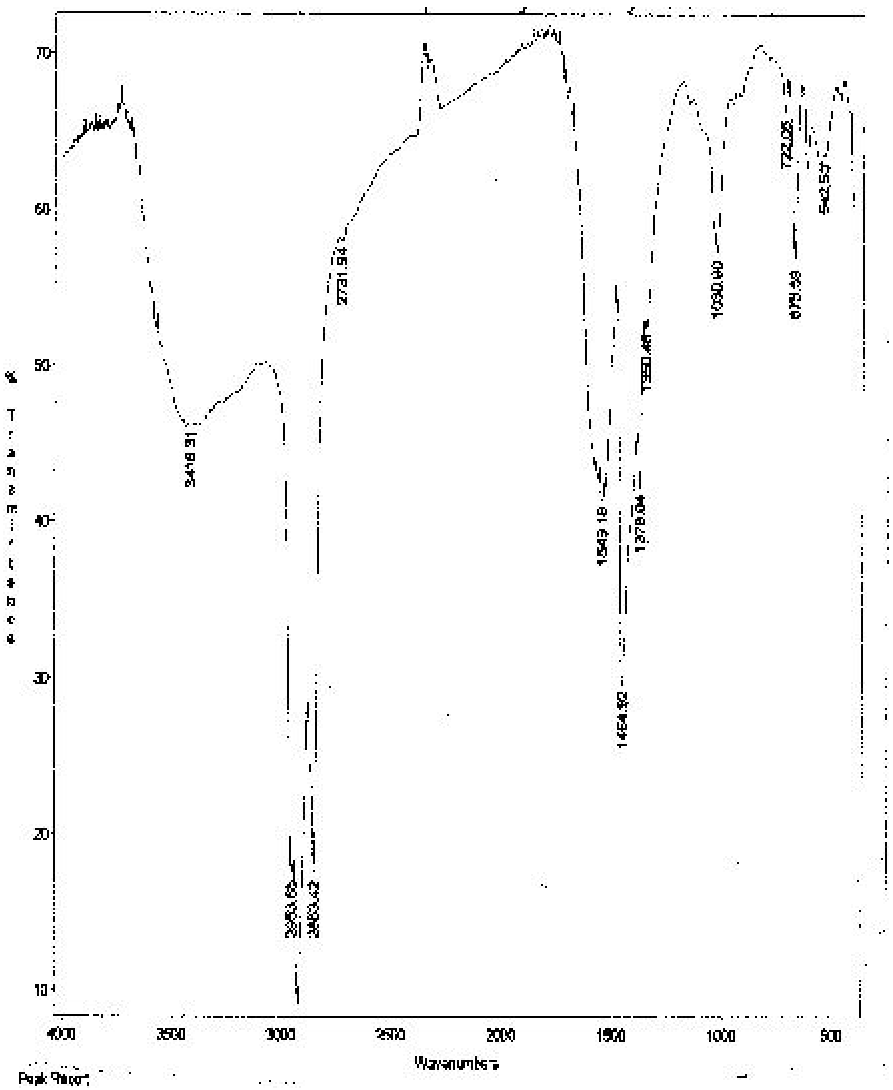

Figure 1: The infrared spectrum of $Cr_2(O_2CCH_3)_4(H_2O)_2$ complex

$Cr_2(O_2CCH_3)_4(H_2O)_2$ complex being compared are quite similar to the ones in Cr(*acac*)$_2$ [17] and $Cr_2(O_2CH)_4(H_2O)_2$ [9] molecules, and in this sense, the use of their force fields to initiate diaquo tetra-μ-acetato dichromium (II) calculations was a good approximation.

The observed **B$_u$** frequencies were satisfactorily reproduced by the final force field listed in Table 2. The fit for groups in the complex is of the same quality as those obtained for same groups in $Cr_2(O_2CH)_4(H_2O)_2$ [9] and $CH_3CO_2^-$ [18]. The force constants of various groups in these molecules and $Cr_2(O_2CCH_3)_4(H_2O)_2$ are compared in Table 4. As anticipated, the agreement between the force constants is good. However, the bridging Cr-O stretching force constant, 2.260990 x 10^5 dyne cm^{-1}, obtained for the $Cr_2(O_2CCH_3)_4(H_2O)_2$ complex is 18% lower than 2.747360 x 10^5 dyne cm^{-1} in $Cr_2(O_2CH)_4(H_2O)_2$ [9]. Thus, the bridging Cr-O bonds in the dichromium (II) acetato complex have less covalent character compared to those in the formato complex. On the contrary, Table 4 shows that COO stretching force constant in the former is about 15% higher than in the latter. Clearly, these seem to indicate that both COO and bridging Cr-O bonds in the two complexes are sensitive to the inductive character and mass of the R group of the RCO_2^- ligand. In fact, because of the close similarity in the magnitude of the difference in the COO and bridging Cr-O force constants, it might be right to infer that the effect of changing R has caused inverse change in the strengths of these bonds.

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