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

* A. Uzairu, G.F.S. Harrison and A. Adamu
Department of Chemistry, Ahmadu Bello University, Zaria-Nigeria.

ABSTRACT

A normal coordinate analysis on diaquo tetra-μ-acetato dichromiun (II) gives calculated frequencies in good agreement with the observed ones in the range 4000 and 400cm^{-1} for the out-of-plane infrared active vibrations of the complex. In order to make theoretical band assignments and to see the coupling between various modes in each band, the potential energy distribution in each normal vibration was calculated. The results showed that 80.36% of these vibrations lie within the range investigated, including 563 and 543cm^{-1} bands assigned to asymmetric bridging Cr-O stretching vibrations.

* Author for correspondence

INTRODUCTION

It was recently observed [1] that past investigations on the infrared spectra of diaquo tetra-μ-acetato dichromium (II) complex were restricted to vibrations localized on the ligands only, and that no information was available on the Cr-Cr and bridging Cr-O stretching vibrations of the complex. In a previous paper of this series [2], however, we have described the in-plane vibrations of this complex that are active in the infrared based on a normal coordinate analysis in which bridging symmetric stretching motions of Cr-O bonds were included. All the four bridging symmetric Cr-O stretching vibrations were shown to be degenerate and assignable to a band at 623cm^{-1}. Comparing the results of that study with those obtained for diaquo tetra-μ-formato dichromium (II) complex earlier reported [3], it was further concluded that the strengths of COO and bridging Cr-O bonds in $Cr_2(O_2CR)_4(H_2O)_2$ (R = H and CH_3) complexes are inversely related.

Also, it should be noted that diaquo tetra-μ-acetato dichromium (II) complex has many out-of-plane vibrations. To complete the infrared spectral investigations on the complex, normal coordinate analysis must similarly be done on the out-of-plane vibrations, especially the asymmetric bridging Cr-O stretching modes, in order to assign them theoretically to observed bands. This paper, therefore, deals with the normal coordinate calculations of the frequencies and associated force constants of the out-of-plane vibrations of the diaquo tetra-μ-acetato dichromium (II) complex that are active in the infrared.

EXPERIMENTAL

(a) Preparation of complex and spectral measurements

The preparation of and infrared spectral measurements on the diaquo tetra-μ-acetato dichromium (II) complex, $Cr_2(O_2CCH_3)_4(H_2O)_2$, together with the absorption curve, were reported previously [2]. However, some of the observed frequencies are presented in Table 1.

(b) Calculations

The number, representations spanned and the internal coordinates describing the out-of-plane vibrations of the $Cr_2(O_2CCH_3)_4(H_2O)_2$ complex were given in ref. 2. Since the complex has a $\mathbf{C_{2h}}$ site symmetry in the solid, its out-of-plane vibrations were found to be grouped into two classes, $23\mathbf{B_g} + 22\mathbf{A_u}$. It was also identified that only the $22\mathbf{A_u}$ motions are active in the infrared. Thus only the vibrations belonging to the $\mathbf{A_u}$ class need be considered for out-of-plane infrared spectral band assignments of the complex.

The elements of the **G** matrix for the $\mathbf{A_u}$ class of out-of-plane vibrations of the complex were calculated using Wilson's method [4]. Transferable valence force field was employed and the conventions of Hollenstein and co-workers [5] were followed in

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

	Observed freq.	Calculated Freq.	Potential energy distribution*	Assignment
1. υ_{52}	2953.65_{vs}	2954.67	$S_{52}(99.99)$	$\upsilon_{as}'(CH_3)$
2. υ_{53}	1571.65_{s}	1571.93	$S_{53}(93.71)$, $S_{58}(6.29)$	$\upsilon_{as}'(COO)$
3. υ_{54}	542.50_{m}	540.39	$S_{54}(99.17)$	$\upsilon_{as}'(OCrO)$
4. υ_{55}	$596.06_{m,sh}$	596.37	$S_{55}(98.59)$, $S_{59}(1.25)$	$\upsilon_{as}'(Cr\text{-}O) + \upsilon_{as}'(OCrO)$
5. υ_{56}	3416.31_{m}	3419.04	$S_{56}(99.99)$	$\upsilon_{as}'(H_2O)$
6. υ_{57}	2953.65_{vs}	2948.46	$S_{57}(99.99)$	$\upsilon_{as}'(CH_3)$
7. υ_{58}	1571.65_{s}	1571.65	$S_{53}(6.29)$, S_{58} (93.71)	$\upsilon_{as}'(COO)$
8. υ_{59}	562.20_{m}	571.36	$S_{55}(1.14)$, $S_{59}(98.86)$	$\upsilon_{as}'(OCrO) + \upsilon_{as}(Cr\text{-}O)$
9. υ_{60}	$1414.96_{m,sh}$	1417.52	$S_{60}(96.97)$, $S_{69}(1.78)$	$\delta_{as}'(CH_3) + \tau_{as}''(CH_3COO)$
10. υ_{61}	743.84_{w}	742.61	$S_{60}(1.35)$, $S_{61}(77.08)$, $S_{62}(15.51)$, $S_{69}(5.43)$	$r_{as}'(C\text{-}C) + \delta_{as}'(Ring) + \tau_{as}''(CH_3COO) + \delta_{as}'(CH_3)$
11. υ_{62}	502.86_{w}	504.00	$S_{54}(2.45)$, $S_{59}(2.11)$, $S_{61}(4.49)$, $S_{62}(89.16)$, $S_{66}(1.69)$	$\delta_{as}'(Ring) + r_{as}'(C\text{-}C) + \upsilon_{as}'(OCrO)$
12. υ_{63}	1653.20_{m}	1653.68	$S_{56}(2.85)$, $S_{63}(97.01)$	$\delta_{as}(H_2O) + \upsilon_{as}'(H_2O)$
13. υ_{64}	$1047.80_{m,sh}$	1048.98	$S_{64}(19.71)$, $S_{69}(79.40)$	$\tau_{as}''(CH_3COO) + r_{as}'(CH_3)$
14. υ_{65}	1351.04_{m}	1355.30	$S_{65}(96.68)$, $S_{72}(2.34)$	$\delta_{as}'(CH_3) + \tau_{as}''(CH_3COO)$
15. υ_{66}	517.04_{w}	521.95	$S_{54}(13.56)$, $S_{59}(2.59)$, $S_{62}(2.57)$, $S_{66}(40.49)$, $S_{67}(39.20)$	$r_{as}'(C\text{-}C) + \delta_{as}'(Ring) + \upsilon_{as}'(OCrO)$
16. υ_{67}	448.82_{w}	443.04	$S_{66}(18.89)$, $S_{67}(78.57)$	$\delta_{as}'(Ring) + r_{as}'(C\text{-}C)$
17. υ_{68}	$1047.80_{m,sh}$	1047.28	$S_{68}(28.15)$, $S_{72}(70.97)$	$\tau_{as}''(CH_3COO) + r_{as}'(CH_3)$
18. υ_{69}	1030.90_{m}	1032.40	$S_{64}(25.55)$, $S_{69}(73.80)$	$\tau_{as}''(CH_3COO) + r_{as}'(CH_3)$
19. υ_{70}	-	78.49	$S_{54}(5.61)$, $S_{59}(5.61)$, $S_{70}(42.83)$, $S_{73}(44.85)$	$r_{as}(OCrO) + \upsilon_{as}'(OCrO)$
20. υ_{71}	1095.21_{w}	1094.52	$S_{71}(99.99)$	$\tau_{as}(H_2O)$
21. υ_{72}	1030.90_{m}	1032.09	$S_{68}(12.91)$, $S_{72}(86.86)$	$\tau_{as}''(CH_3COO) + r_{as}'(CH_3)$
22. υ_{73}	-	87.19	$S_{70}(51.11)$, $S_{73}(48.89)$	$r_{as}(OCrO)$

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

* For the meaning of the internal coordinates, S_I, I = 52 – 73, see ref. 1.

setting up the **F** matrix. The application of those criteria left 45 distinct force constants. The force fields of $Cr_2(O_2CH)_4(H_2O)_2$ [3] and CH_3COO^- ion [5] were used to start the calculations. Then, matrix secular equations, $|\mathbf{GF} - E\Lambda| = 0$, were solved. The calculations were made with the aid of molecular dimensions given in ref. 3. 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 computed and observed values is quite satisfactory, although the bands corresponding to the calculated frequencies of 87 and 79 cm^{-1} were not observed because they were outside the 4000 – 400 cm^{-1} covered by our investigation. Finally, the potential energy distribution in each out-of-plane normal mode was calculated with respect to each internal coordinate in order to make theoretical band assignments [6] and to determine the mixing ratio of various normal modes in each band.

RESULTS AND DISCUSSION

In Table 1 the observed frequencies are compared with the values calculated by normal coordinate analysis. The agreements are quite good for such a complicated ring system, although the bands corresponding to 77 and 86cm^{-1} could not be observed because these frequencies were outside of our observable region.

The $Cr_2(O_2CCH_3)_4(H_2O)_2$ complex has 45 out-of-plane normal vibrations [1] which are grouped into 23$\mathbf{B_g}$ + 22$\mathbf{A_u}$ classes. These are made up of (6$\mathbf{B_g}$ + 6$\mathbf{A_u}$) CH_3, (2$\mathbf{B_g}$ + 2$\mathbf{A_u}$) C-C, (2$\mathbf{B_g}$ + 2$\mathbf{A_u}$)COO, (4$\mathbf{B_g}$ +

4$\mathbf{A_u}$)OCrO, ($\mathbf{B_g}$ + $\mathbf{A_u}$)Cr-O, (2$\mathbf{B_g}$ + 3$\mathbf{A_u}$)H_2O, (2$\mathbf{B_g}$ + 2$\mathbf{A_u}$) Ring and (4$\mathbf{B_u}$ + 2$\mathbf{A_u}$)CH_3COO vibrational modes. However, as mentioned earlier, only those out-of-plane vibrations belonging to the $\mathbf{A_u}$ representation are active in the infrared. In fact, 19 of the 22Au bands have been

Table 2: Force constants (x 10^5 dyne cm^{-1}) of $Cr_2(O_2CCH_3)_4(H_2O)_2$ complex

A. Diagonal Force constants

	Coordinate	Value
1.	$\upsilon_{as}'(CH_3)$	4.658227
2.	$\upsilon_{as}'(COO)$	7.527143
3.	$\upsilon_{as}'(OCrO)$	2.774413
4.	$\upsilon_{as}'(Cr\text{-}O)$	2.560922
5.	$\upsilon_{as}'(H_2O)$	6.520085
6.	$\delta_{as}'(CH_3)$	0.434991
7.	$r_{as}'(C\text{-}C)$	0.320481
8.	$\delta_{as}'(Ring)$	0.627959
9.	$\delta_{as}(H_2O)$	0.414622
10.	$r_{as}'(CH_3)$	0.289096
11.	$\tau_{as}''(CH_3COO)$	1.207417
12.	$r_{as}(OCrO)$	0.06005
13.	$\tau_{as}(H_2O)$	0.712307

B. Interaction force constants

	Coordinates		Value
14.	$r_{as}'(C\text{-}C)$	$\delta_{as}'(Ring)$	0.059873
15.		$r_{as}'(CH_3)$	0.007810
16.		$\tau_{as}''(CH_3COO)$	-0.008653
17.	$\delta_{as}'(Ring)$	$\delta_{as}'(Ring)$	0.020402
18.		$\tau_{as}''(CH_3COO)$	0.012811
19.		$r_{as}(OCrO)$	0.017423
20.	$\delta_{as}(H_2O)$	$\tau_{as}(H_2O)$	-0.027621
21.	$r_{as}'(CH_3)$	$\tau_{as}''(CH_3COO)$	0.010834
22.	$\tau_{as}''(CH_3COO)$	$r_{as}(OCrO)$	0.014328

B. Interaction force constants cont'd

	Coordinates		Value
23.	$\upsilon_{as}'(CH_3)$	$\delta_{as}'(CH_3)$	0.054372
24.		$r_{as}'(C\text{-}C)$	0.097198
25.		$r_{as}'(CH_3)$	0.015834
26.		$\tau_{as}''(CH_3COO)$	0.021702
27.	$\upsilon_{as}'(COO)$	$\upsilon_{as}'(OCrO)$	0.064621
28.		$r_{as}'(C\text{-}C)$	0.001752
29.		$\delta_{as}'(Ring)$	0.032987
30.		$\tau_{as}''(CH_3COO)$	0.088217
31.		$r_{as}(OCrO)$	0.006128
32.	$\upsilon_{as}'(OCrO)$	$\upsilon_{as}(Cr\text{-}O)$	0.021576
33.		$\delta_{as}'(Ring)$	0.045044
34.		$\tau_{as}''(CH_3COO)$	0.137581
35.		$r_{as}(OCrO)$	0.075380
36.	$\upsilon_{as}(Cr\text{-}O)$	$\upsilon_{as}'(H_2O)$	0.016351
37.		$\delta_{as}'(Ring)$	0.006531
38.		$\delta_{as}(H_2O)$	0.007983
39.		$\tau_{as}(H_2O)$	0.042763
40.		$r_{as}(OCrO)$	0.008874
41.	$\upsilon_{as}'(H_2O)$	$\delta_{as}(H_2O)$	0.216289
42.		$\tau_{as}(H_2O)$	0.031830
43.	$\delta_{as}'(CH_3)$	$r_{as}'(C\text{-}C)$	0.039276
44.		$r_{as}'(CH_3)$	0.008320
45.		$\tau_{as}''(CH_3COO)$	0.018973

Table 3: Force constants (x 10^5 dyne cm^{-1}) for some groups in the $Cr(O_2CCH_3)_4(H_2O)_2$ complex compared with values known for closer molecules/fragments

Coordinate(s)	values		
	$Cr_2(O_2CH)_4(H_2O)_2$ [a]	CH_3COO^- [b]	$Cr_2(O_2CCH_3)_4(H_2O)_2$
$\upsilon_{as}'(CH_3)$	4.513306	4.848564	4.638227
$\upsilon_{as}'(COO)$	7.633842	7.581072	7.527143
$\upsilon_{as}'(OCrO)$	2.374062		2.774413
$\upsilon_{as}(Cr\text{-}O)$	2.566425		2.566922
$\upsilon_{as}'(H_2O)$	6.336049		6.520086
$\delta_{as}'(CH_3)$	0.449008		0.434991
$\delta_{as}'(Ring)$	0.421494		0.627959
$r_{as}'(CH_3)$	0.279014		0.289096
$\tau_{as}''(CH_3COO)$		1.220116	1.207417
$\upsilon_{as}'(OCrO)$ $\delta_{as}'(Ring)$	0.043754		0.045044
$\delta_{as}'(Ring)$ $\delta_{as}'(Ring)$	0.019402		0.020402
$\upsilon_{as}'(COO)$ $\delta_{as}'(Ring)$	0.027519		0.032987

[a] ref. - 3 ; [b] ref. - 5

observed and theoretically assigned. These include a band at 2954cm^{-1}, which is due to doubly degenerate pure $\upsilon_{as}'(CH_3)$ stretching modes, and the bands at 1415, 1351 and 1048 cm^{-1}. The first two of these bands are due to two $\delta_{as}'(CH_3)$ vibrations with 1.78 and 2.34% contributions from $\tau_{as}''(CH_3COO)$ mode while the 1048cm^{-1} band represents the frequencies of two mixed out-of-plane vibrations made up of $r_{as}'(CH_3)$ and $\tau_{as}''(CH_3COO)$ modes.

The bands at 744 and 517cm^{-1} were also assigned to r_{as}'(C-C) coupled with δ_{as}'(ring), $\tau_{as}''(CH_3COO)$ and $\delta_{as}'(CH_3)$ modes and r_{as}'(C-C) coupled with δ_{as}'(ring) and υ_{as}'(OCrO) modes, respectively. The 2**A$_u$** COO motions are pure and degenerate, and are described by the band at 1572cm^{-1}. However, only 2 of the 4 **A$_u$** bridging Cr-O bands were observed. They are located at 562 and 543 cm^{-1}, and were assigned to υ_{as}'(OCrO) coupled with υ_{as} (Cr-O) and υ_{as}'(OCrO) vibrations, respectively. The axial Cr-O bonds have only one motion, which is υ_{as}(Cr-O), belonging to the **A$_u$** representation. It is assigned to the band at 596 cm^{-1}, and was found to mix with υ_{as}'(OCrO) mode.

The two axial H_2O ligands of the complex have one stretching, one deformation and one torsional vibrations belonging to the **A$_u$** class. The positions of the bands describing these motions are located at 3416, 1653 and 1095 cm^{-1}, and, are due, respectively, to $\upsilon_{as}'(H_2O)$, $\delta_{as}(H_2O)$ with 2.85% contribution from $\upsilon_{as}'(H_2O)$ and τ_{as} (H_2O) modes. The asymmetric rocking vibrations of the COO groups of the 4 bridging CH_3-CO_2^- ligands give rise to 2 **A$_u$** out-of-plane Ring deformations. However, they couple with other vibrations and are assignable to the bands at 503 and 449cm^{-1}. Lastly the band at 1031 cm^{-1} completes the list of the nineteen **A$_u$** bands observed for the $Cr_2(O_2CCH_3)_4(H_2O)_2$ complex; it describes a pair of degenerate CH_3COO torsion vibrations coupled with $r_{as}'(CH_3)$ mode. The assignments of the 22Au out-of-plane vibrations of the $Cr_2(O_2CCH_3)_4(H_2O)_2$ complex in this study agree very well with similar vibrations assigned previously for $Cr_2(O_2CH)_4(H_2O)_2$ [3] and $CH_3CO_2^-$ ion [5] on the basis of normal coordinate treatments.

The final force field listed in Table 2 satisfactorily reproduced the observed **A$_u$** frequencies. As expected, the fit for some groups in the complex is of the same quality as those obtained for same groups in $Cr_2(O_2CH)_4(H_2O)_2$ [3] and $CH_3CO_2^-$ ion [5]. However, the $\upsilon_{as}'(CH_3)$ stretching force constant, 4.658227 x 10^5 dyne cm^{-1}, obtained for the $Cr_2(O_2CCH_3)_4(H_2O)_2$ complex is 4% smaller than 4.8485564 x 10^5 dyne cm^{-1} in CH_3COO^- ion [5]. Thus, the C-H bonds of the methyl group in the latter are slightly stronger compared to those in the tetra-μ-acetato dichromium (II) complex. Similarly, υ_{as}'(OCrO) stretching force constant in the tetra-μ-acetato complex is about 17% greater than that obtained for $Cr_2(O_2CH)_4(H_2O)_2$ complex [3]. Likewise, $\upsilon_{as}'(H_2O)$ force constant is a little greater in this complex than in the tetra-μ-formato dichromium (II) complex. In spite of these small variations (Table 3), agreement between the force constants of the complex under study with similar ones in $Cr_2(O_2CH)_4(H_2O)_2$ and CH_3COO^- is quite good implying that the transfer of some force constants in these molecules to initialize $Cr_2(O_2CCH_3)_4(H_2O)_2$ calculations was reasonable.

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