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NORMAL COORDINATE TREATMENT ON THE DIAQUO TETRA-μ-FORMATO DICHROMIUM (II) COMPLEX IN THE SOLID STATE. III. INFRARED SPECTRAL BAND ASSIGNMENTS FOR THE IN-PLANE VIBRATIONS OF THE COMPLEX

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ABSTRACT

Normal coordinate calculations have been done in order to describe all the in-plane normal vibrations of the $Cr_2(O_2CH)_4(H_2O)_2$ complex. Theoretical band assignments were made and the mixing ratio of various modes in each band determined. The results show that strong coupling occurs between ν_s(OCrO), ν(Cr-Cr), δ_s(ring) and δ_s'(ring) on the one hand, and δ_{as}(ring), r_{as}(C-H) and ν_{as}(OCrO) on the other in a number of the normal vibrations. Also, the existence of multiples of electronically identical groups in the complex lead to many double and triple accidental degeneracies.

KEYWORDS: In-plane vibrations, theoretical band assignments, coupling between normal modes, accidental degeneracies and normal coordinate treatment

INTRODUCTION

The vibrational spectra of the quadruply bonded $M_2(O_2CR)_4L_2$ complexes (where M = transition metal atom; R = H, CH_3, C_2H_5, etc.; L = neutral ligand) have been measured (Clark et al., 1992; Martin et al., 1982; Miskowski et al., 1987; Clark and Hempleman, 1989, Clark et al., 1988*a*; Santure et al., 1985, and Cotton and Norman, 1972) because of the relationships between the M-M and bridging M-O bond stretching frequencies and the stabilities and structures of the complexes. However, most of the past vibrational investigations list the infrared or Raman absorption frequencies of the complexes only, with the M-M and bridging M-O stretching bands being the mostly assigned (Clark et al., 1988*b*; Clark and Ferris, 1981; Oldham *et al.*, 1971; and Garner et al., 1976). Although the possibility of considerable mixing of the M-M and bridging M-O stretching modes with other normal modes was since observed (Hutchinson et al., 1979; Bratton et al., 1971, and Ketteringham et al., 1976), there has been nearly complete absence of normal coordinate treatments of the vibrations of these complexes. Such studies could theoretically confirm the assignments of the M-M and the bridging M-O vibrations as well as infer the extent of coupling between the M-M, bridging M-O and other internal displacement coordinates. To date, only four incomplete attempts to carry out such theoretical band assignments are recorded in the literature (Bratton et al., 1971; Ketteringham et al., 1976; and Uzairu et al., 2003).

For $Cr_2(O_2CR)_4L_2$ complexes, no complete theoretical band assignments of the vibrational spectra of any one of them exist at the present time. In our previous article (Uzairu et al., 2003) of this series, however, the solid state infrared spectrum of $Cr_2(O_2CH)_4(H_2O)_2$ was partially interpreted using normal coordinate analysis for the first time. In order to simplify the calculations, we simulated the complex by a 1:1 (Cr_2^{4+} $HCOO^-$) model and, on this basis, made theoretical assignments of the Cr-Cr and bridging Cr-O bands.

Nevertheless, it was shown (Uzairu et al., 2004) that such a 1:1 complex approximation could describe only 18% of the normal vibrations of the complex. In addition, ligand - ligand interactions are absent in the model thus concealing any information regarding coupling of their internal coordinates.

In order to describe all the normal vibrations of the $Cr_2(O_2CH)_4(H_2O)_2$ complex as well as fully infer the extent of coupling between all the modes, we have undertaken to carry out normal coordinate treatments on the whole complex. $Cr_2(O_2CH)_4(H_2O)_2$ has 66 normal modes of vibration, and, in the first part of the full investigation (Uzairu et al., 2004*a*), we reported the calculations of the 66 genuine internal coordinates of the complex that describe the 66 normal vibrations and their assignments to vibrational modes. These were shown to be partitioned into $23A_1 + 7B_1 + 13B_2$ in-plane and $9A_2 + 9B_1 + 5B_2$ out-of-plane orthogonal vibrations. In the second part (Uzairu et al., 2004*b*), normal coordinate calculations and theoretical band assignments of all the $9A_2 + 9B_1 + 5B_2$ out-of-plane vibrations of the complex were made.

The present work, being a continuation as well as complementary to the past investigations (Uzairu et al., 2004*a*,*b*) on the complex, was carried out in order to describe the $23A_1 + 7B_1 + 13B_2$ in-plane vibrations based on normal coordinate analysis and to theoretically assign them to observed bands of the complex. Transferable valence force field was employed in the calculations. This initiates a force constant bank and allows the force constants to be transferable between varieties of similar molecules.

EXPERIMENTAL

(*a*) *Preparation of Complex and Spectral Measurements*

The preparation of and infrared spectral measurements on the diaquo tetra-μ-formato dichromium (II) complex, $Cr_2(O_2CH)_4(H_2O)_2$, together with the absorption curve, were reported elsewhere (Uzairu et al., 2003). However, some of the observed frequencies are shown in Table 1.

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Table 1. Comparison of observed and calculated frequencies of $Cr_2(O_2CH)_4(H_2O)_2$ complex (cm^{-1})

Species	Obs. Freq.[1]	Calc. Freq.	Potential energy distribution	assignment
A_1 (symmetric in-plane motions of the groups on both molecular planes I and II of the $Cr_2(O_2CH)_4(H_2O)_2$ complex, and the modes have been so identified with their planes)				
υ_1	2854.56vs	2855.27	$S_1(99.99)$	ν_s(C-H) I
υ_2	1351.24s.sh	1350.39	$S_2(99.67)$	ν_s(COO) I
υ_3	1462.81s	1463.38	$S_3(64.57)$, $S_{18}(34.66)$	ν_s' (COO) I + ν_s' (COO) II
υ_4	547.38m	543.10	$S_5(47.15)$, $S_6(40.74)$, $S_4(7.58)$, $S_{15}(3.31)$	ν_s(OCrO) I + ν(Cr-Cr) I + δ_s' (ring) I
υ_5	540.09m	540.58	$S_4(59.31)$, $S_5(27.53)$, $S_6(8.72)$, $S_{15}(2.60)$, $S_{20}(1.44)$	ν_s(OCrO) I + ν(Cr-Cr) I + ν_s(OCrO) II
υ_6	537.59m	536.50	$S_6(68.25)$, $S_4(19.82)$, $S_5(8.47)$, $S_{23}(1.68)$, $S_{19}(1.63)$	ν(Cr-Cr) I + ν_s(OCrO) I + ν_s(OCrO) II
υ_7	596.07m	596.72	$S_8(49.83)$, $S_7(49.80)$	ν(Cr-O) I
υ_8	596.07m	596.70	$S_7(50.00)$, $S_8(49.99)$	ν(Cr-O) I
υ_9	3374.80vs	3340.96	$S_9(99.98)$	ν_s(O-H) I
υ_{10}	3392.48vs	3394.93	$S_{10}(99.97)$	ν_s(O-H) I
υ_{11}	654.31w	649.51	$S_{11}(78.17)$, $S_{21}(9.19)$, $S_6(4.30)$, $S_7(2.60)$, $S_8(2.60)$, $S_{15}(1.09)$, $S_{23}(0.94)$	δ_s(ring) I + δ_s(ring) II + ν(Cr-Cr) I + (Cr-O) I + δ_s' (ring) I + δ_s' (ring) II
υ_{12}	-	4654.75	$S_{12}(99.13)$, $S_9(0.82)$	δ(O-H) I + ν_s(O-H) I
υ_{13}	1747.74m	1750.02	$S_{13}(98.62)$, $S_{10}(1.33)$	δ(O-H) I + ν_s(O-H) I
υ_{14}	1378.93s	1378.01	$S_{14}(74.67)$, $S_2(24.61)$	r_s(C-H) I + ν_s(COO) I
υ_{15}	525.38w	510.45	$S_{15}(44.42)$, $S_6(25.67)$, $S_5(13.56)$, $S_4(12.33)$, $S_{23}(1.85)$	δ_s' (ring) I + ν(Cr-Cr) I + ν_s(OCrO) I + δ_s' (ring) II
υ_{16}	2854.56vs	2855.19	$S_{16}(99.98)$	ν_s(C-H) II
υ_{17}	1351.24s.sh	1350.76	$S_{17}(99.72)$	ν_s(COO) II
υ_{18}	1462.81s	1463.38	$S_{18}(64.56)$, $S_3(34.66)$	ν_s' (COO) II + ν_s' (COO) I
υ_{19}	540.09m	540.03	$S_{20}(56.42)$, $S_{19}(43.53)$	ν_s(OCrO) II
υ_{20}	540.09m	541.39	$S_{19}(50.19)$, $S_{20}(38.55)$, $S_5(6.30)$, $S_6(4.25)$	ν_s(OCrO) II + ν_s(OCrO) I + ν(Cr-Cr) I
υ_{21}	670.05w	673.55	$S_{21}(86.62)$, $S_{11}(10.54)$, $S_6(1.01)$	δ_s(ring) II + δ_s(ring) I + ν(Cr-Cr) I
υ_{22}	1009.71m	1016.95	$S_{22}(98.89)$	r_s(C-H) II
υ_{23}	463.64w	461.06	$S_{23}(79.15)$, $S_6(10.94)$, $S_{19}(3.41)$, $S_{20}(3.09)$, $S_{15}(1.74)$	δ_s' (ring) II + ν(Cr-Cr) I + ν_s(OCrO) II + δ_s' (ring) I
B_1 (asymmetric in-plane motions of the groups on the molecular plane II of the $Cr_2(O_2CH)_4(H_2O)_2$ complex)				
υ_{42}	2870.62s.sh	2870.45	$S_{42}(99.99)$	ν_{as}(C-H)
υ_{43}	1582.75vs	1583.18	$S_{43}(99.99)$	ν_{as}(COO)
υ_{44}	639.59w	637.45	$S_{44}(97.98)$, $S_{45}(1.92)$	ν_{as}(OCrO)

Table 1 cont'd

ν_{45}	639.59w	638.55	$S_{45}(97.83)$, $S_{41}(2.03)$	$\nu_{as}(OCrO)$
ν_{46}	1030.67m	1029.60	$S_{46}(98.42)$, $S_{48}(1.26)$	$r_s(C\text{-}H) + \delta_s'(ring)$
ν_{47}	766.96m	762.79	$S_{47}(97.38)$, $S_{45}(1.37)$, $S_{41}(1.00)$	$\delta_s(ring) + \nu_s(OCrO)$
ν_{48}	449.50w	448.04	$S_{48}(98.46)$	$\delta_{as}'(ring)$
B_2 (asymmetric in-plane motions of the groups on the molecular plane I of the $Cr_2(O_2CH)_4(H_2O)_2$ complex)				
ν_{54}	2870.62s.sh	2870.49	$S_{54}(99.99)$	$\nu_{as}(C\text{-}H)$
ν_{55}	1582.75vs	1583.18	$S_{55}(99.99)$	$\nu_{as}(COO)$
ν_{56}	813.20w	815.93	$S_{56}(99.61)$	$\nu_{as}(OCrO)$
ν_{57}	639.59w	637.46	$S_{57}(99.93)$	$\nu_{as}(OCrO)$
ν_{58}	3401.52vs	3405.14	$S_{58}(99.99)$	$\nu_s(O\text{-}H)$
ν_{59}	3374.80vs	3355.47	$S_{59}(99.99)$	$\nu_{as}(O\text{-}H)$
ν_{60}	1392.56s.sh	1392.80	$S_{60}(99.91)$	$r_{as}(C\text{-}H)$
ν_{61}	1132.92m	1138.10	$S_{61}(63.46)$, $S_{58}(36.40)$	$r(H_2O) + \nu_s(O\text{-}H)$
ν_{62}	875.63m	872.04	$S_{62}(61.58)$, $S_{59}(38.32)$	$r(H_2O) + \nu_{as}(O\text{-}H)$
ν_{63}	-	112.61	$S_{63}(48.65)$, $S_{66}(27.58)$, $S_{64}(23.17)$	$r(Cr\text{-}O) + \delta_{as}'(ring)$

Table 1 cont'd

ν_{64}	-	128.83	$S_{64}(65.85)$, $S_{63}(31.93)$, $S_{66}(2.17)$	$r(Cr\text{-}O) + \delta_{as}'(ring)$
ν_{65}	722.34m.sh	741.66	$S_{65}(89.78)$, $S_{56}(8.66)$, $S_{57}(1.31)$	$\delta_{as}(ring) + \nu_{as}(OCrO)$
ν_{66}	449.50w	449.44	$S_{66}(98.87)$	$\delta_{as}'(ring)$

ν, stretching mode. δ, deformation mode. r, rocking mode. s, symmetric. *as*, asymmetric. relative intensities vs, very strong. s, strong. m, medium; w, weak; sh, shoulder

(b) Method of Calculation

The genuine independent internal coordinates of the $23A_1 + 7B_1 + 13B_2$ (43) in-plane vibrations are presented in Tables 2 – 4. They were calculated from elementary coordinates of bond stretching and valence angle bending indicated in Figures 1 – 3. The details of the calculation were already reported in a previous article (Uzairu et al. 2004a) of this series. At present, most authors use transferable valence force field. In order to facilitate a comparison with force fields by other authors and to create a force constant bank for these kinds of complexes, we have adopted this type of valence force field. The F matrices were thus constructed following the conventions of Hollenstein et al. (1983), which are widespread in the literature on the subject. The application of those criteria left 43 distinct force constants for the $Cr_2(O_2CH)_4(H_2O)_2$ complex. Initial force constants for groups in the complex were taken from the force fields of CH_3COO^- ion (Uzairu and Harrison, 2005), H_2O_2 (Arnau and Giguére, 1974) $Cr_2(mhp)_4$ complex (Cotton and Walton, 1993) and Cr(*acac*)$_2$ (Nakamoto and Mwtell, 1960). The elements of **G** matrices for the A_1, B_1 and B_2 classes of the in-plane vibrations of the complex were calculated according to a standard method (Woodward, 1972) described in the literature and matrix secular equations, $|GF - E\lambda| = 0$, solved for each of the classes

Table 2. The genuine $23A_1$ (in-plane) internal coordinates

Internal coordinate	Vibrational mode
$S_1 = \frac{1}{\sqrt{2}}(\Delta D_1 + \Delta D_2)$	$\upsilon_s(C-H)$
$S_2 = \frac{1}{2}\{(\Delta d_1 + \Delta d_2) + (\Delta d_3 + \Delta d_4)\}$	$\upsilon_s(COO)$
$S_3 = \frac{1}{2}\{(\Delta d_1 - \Delta d_2) + (\Delta d_3 - \Delta d_4)\}$	$\upsilon'_s(COO)$
$S_4 = \frac{1}{\sqrt{2}}(\Delta r_1 + \Delta r_3)$	$\upsilon_s(OCrO)$
$S_5 = \frac{1}{\sqrt{2}}(\Delta r_2 + \Delta r_4)$	$\upsilon_s(OCrO)$
$S_6 = \Delta R$	$\upsilon(Cr-Cr)$
$S_7 = \Delta h_1$	$\upsilon(Cr-O)$
$S_8 = \Delta h_2$	$\upsilon(Cr-O)$
$S_9 = \frac{1}{\sqrt{2}}(\Delta b_1 + \Delta b_2)$	$\upsilon_s(O-H)$
$S_{10} = \frac{1}{\sqrt{2}}(\Delta b_3 + \Delta b_4)$	$\upsilon_s(O-H)$
$S_{11} = \frac{1}{20^{\frac{1}{2}}}\{(\Delta\beta_1 + \Delta\beta_2 - 2\Delta\varepsilon_1 + \Delta\delta_1 + \Delta\delta_2 - \Delta\alpha_1 - \Delta\alpha_2 + \Delta\phi_1 + \Delta\phi_3)$ $+ (\Delta\beta_3 + \Delta\beta_4 - 2\Delta\varepsilon_2 + \Delta\delta_3 + \Delta\delta_4 - \Delta\alpha_3 - \Delta\alpha_4 + \Delta\phi_2 + \Delta\phi_4)\}$	$\delta_s(ring)$
$S_{12} = \frac{1}{2}(\Delta\eta_1 + \Delta\eta_2 - 2\Delta\Omega_1)$	$\delta(O-H)$
$S_{13} = \frac{1}{2}(\Delta\eta_3 + \Delta\eta_4 - 2\Delta\Omega_2)$	$\delta(O-H)$
$S_{14} = \frac{1}{2}\{(\Delta\beta_1 - \Delta\beta_2) + (\Delta\beta_3 - \Delta\beta_4)\}$	$r_s(C-H)$
$S_{15} = \frac{1}{12^{\frac{1}{2}}}\{(\Delta\delta_1 - \Delta\delta_2 - \Delta\alpha_1 + \Delta\alpha_2 + \Delta\phi_1 - \Delta\phi_3)$ $+ (\Delta\delta_3 - \Delta\delta_4 - \Delta\alpha_3 + \Delta\alpha_4 + \Delta\phi_2 - \Delta\phi_4)\}$	$\delta'_s(ring)$
$S_{16} = \frac{1}{\sqrt{2}}(\Delta D'_1 + \Delta D'_2)$	$\upsilon_s(C-H)$
$S_{17} = \frac{1}{2}\{(\Delta d'_1 + \Delta d'_2) + (\Delta d'_3 + \Delta d'_4)\}$	$\upsilon_s(COO)$
$S_{18} = \frac{1}{2}\{(\Delta d'_1 - \Delta d'_2) + (\Delta d'_3 - \Delta d'_4)\}$	$\upsilon'_s(COO)$

Table 2 continued

$S_{19} = \frac{1}{\sqrt{2}}(\Delta r'_1 + \Delta r'_3)$	$\upsilon_s(OCrO)$
$S_{20} = \frac{1}{\sqrt{2}}(\Delta r'_2 + \Delta r'_4)$	$\upsilon_s(OCrO)$
$S_{21} = \frac{1}{20^{\frac{1}{2}}}\{(\Delta\beta'_1 + \Delta\beta'_2 - 2\Delta\varepsilon'_1 + \Delta\delta'_1 + \Delta\delta'_2 - \Delta\alpha'_1 - \Delta\alpha'_2 + \Delta\phi'_1 + \Delta\phi'_3)$ $+ (\Delta\beta'_3 + \Delta\beta'_4 - 2\Delta\varepsilon'_2 + \Delta\delta'_3 + \Delta\delta'_4 - \Delta\alpha'_3 - \Delta\alpha'_4 + \Delta\phi'_2 + \Delta\phi'_4)\}$	$\delta_s(ring)$
$S_{22} = \frac{1}{2}\{(\Delta\beta'_1 - \Delta\beta'_2) + (\Delta\beta'_3 - \Delta\beta'_4)\}$	$r_s(C-H)$
$S_{23} = \frac{1}{12^{\frac{1}{2}}}\{(\Delta\delta'_1 - \Delta\delta'_2 - \Delta\alpha'_1 + \Delta\alpha'_2 + \Delta\phi'_1 - \Delta\phi'_3)$ $+ (\Delta\delta'_3 - \Delta\delta'_4 - \Delta\alpha'_3 + \Delta\alpha'_4 + \Delta\phi'_2 - \Delta\phi'_4)\}$	$\delta'_s(ring)$

Table 3. The genuine $7B_1$ in-plane internal coordinates

Internal coordinate	Vibrational mode
$S_{42}=\frac{1}{\sqrt{2}}(\Delta D'_1-\Delta D'_2)$	$\upsilon_{as}(C-H)$
$S_{43}=\frac{1}{2}\{(\Delta d'_1-\Delta d'_2)-(\Delta d'_3-\Delta d'_4)\}$	$\upsilon_{as}(COO)$
$S_{44}=\frac{1}{\sqrt{2}}(\Delta r'_1-\Delta r'_3)$	$\upsilon_{as}(OCrO)$
$S_{45}=\frac{1}{\sqrt{2}}(\Delta r'_2-\Delta r'_4)$	$\upsilon_{as}(OCrO)$
$S_{46}=\frac{1}{2}\{(\Delta\beta'_1-\Delta\beta'_2)-(\Delta\beta'_3-\Delta\beta'_4)\}$	$r_{as}(C-H)$
$S_{47}=\frac{1}{16^{\frac{1}{2}}}\{(\Delta\beta'_1+\Delta\beta'_2-2\Delta\varepsilon'_1+\Delta\delta'_1+\Delta\delta'_2-\Delta\alpha'_1-\Delta\alpha'_2)$ $-(\Delta\beta'_3+\Delta\beta'_4-2\Delta\varepsilon'_2+\Delta\delta'_3+\Delta\delta'_4-\Delta\alpha'_3-\Delta\alpha'_4)\}$	$\delta_{as}(ring)$
$S_{48}=\frac{1}{8^{\frac{1}{2}}}\{(\Delta\delta'_1-\Delta\delta'_2-\Delta\alpha'_1+\Delta\alpha'_2)-(\Delta\delta'_3-\Delta\delta'_4-\Delta\alpha'_3+\Delta\alpha'_4)\}$	$\delta'_{as}(ring)$

Table 4. The genuine $13B_2$ in-plane internal coordinates

Internal coordinate	Vibrational mode
$S_{54}=\frac{1}{\sqrt{2}}(\Delta D_1-\Delta D_2)$	$\upsilon_{as}(C-H)$
$S_{55}=\frac{1}{2}\{(\Delta d_1-\Delta d_2)-(\Delta d_3-\Delta d_4)\}$	$\upsilon_{as}(COO)$
$S_{56}=\frac{1}{\sqrt{2}}(\Delta r_1-\Delta r_3)$	$\upsilon_{as}(OCrO)$
$S_{57}=\frac{1}{\sqrt{2}}(\Delta r_2-\Delta r_4)$	$\upsilon_{as}(OCrO)$
$S_{58}=\frac{1}{\sqrt{2}}(\Delta h_1-\Delta h_2)$	$\upsilon_{as}(O-H)$
$S_{59}=\frac{1}{\sqrt{2}}(\Delta h_3-\Delta h_4)$	$\upsilon_{as}(O-H)$
$S_{60}=\frac{1}{2}\{(\Delta\beta_1-\Delta\beta_2)-(\Delta\beta_3-\Delta\beta_4)\}$	$r_{as}(C-H)$
$S_{61}=\frac{1}{\sqrt{2}}(\Delta\eta_1-\Delta\eta_2)$	$r(H_2O)$
$S_{62}=\frac{1}{\sqrt{2}}(\Delta\eta_3-\Delta\eta_4)$	$r(H_2O)$
$S_{63}=\frac{1}{\sqrt{2}}(\Delta\phi_1-\Delta\phi_2)$	$r(Cr-O)$
$S_{64}=\frac{1}{\sqrt{2}}(\Delta\phi_3-\Delta\phi_4)$	$r(Cr-O)$
$S_{65}=1/16^{1/2}\{(\Delta\beta_1+\Delta\beta_2-2\Delta\varepsilon_1+\Delta\delta_1+\Delta\delta_2-\Delta\alpha_1-\Delta\alpha_2)$ $-(\Delta\beta_3+\Delta\beta_4-2\Delta\varepsilon_2+\Delta\delta_3+\Delta\delta_4-\Delta\alpha_3-\Delta\alpha_4)\}$	$\delta_{as}(ring)$
$S_{66}=1/8^{1/2}\{(\Delta\delta_1-\Delta\delta_2-\Delta\alpha_1+\Delta\alpha_2)-(\Delta\delta_3-\Delta\delta_4-\Delta\alpha_3+\Delta\alpha_4)\}$	$\delta'_{as}(ring)$

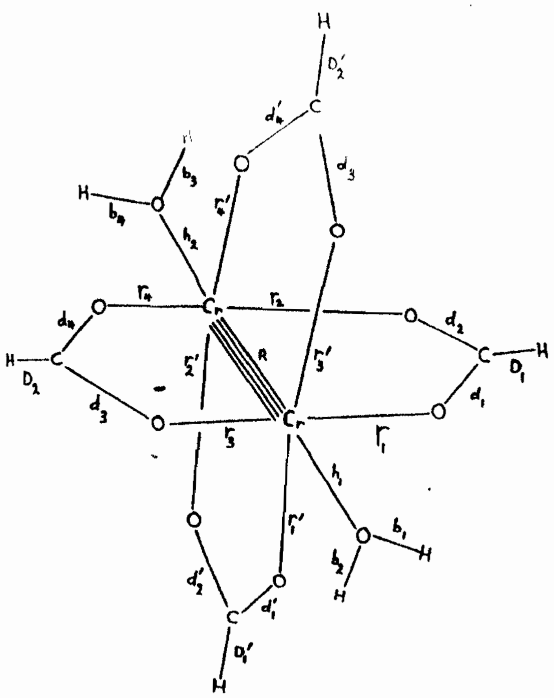

Fig 1 Elementary coordinates of bond stretching of the $Cr_2(O_2CH)_4(H_2O)_2$ complex

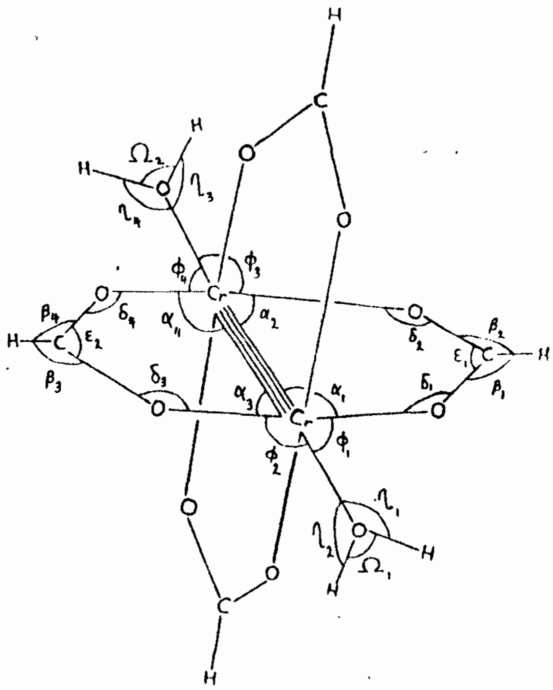

Fig. 2. Elementary coordinates of valence angle bending for groups that are on the σ(yz) plane of the $Cr_2(O_2CH)_4(H_2O)_2$ complex

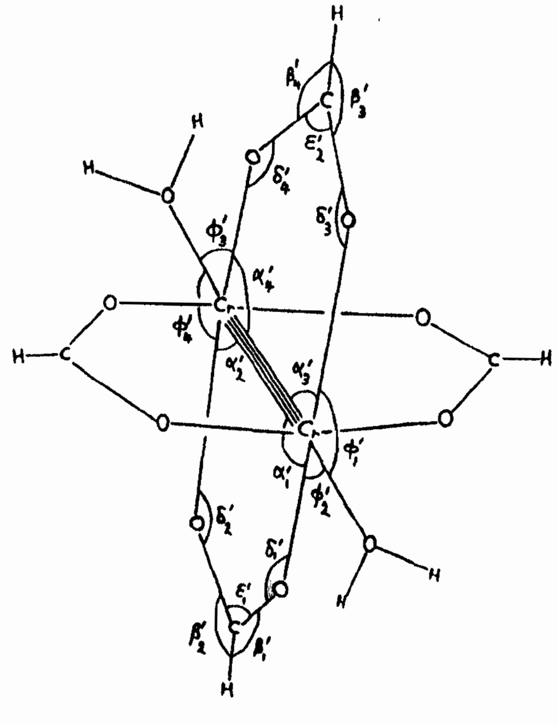

Fig. 3 Elementary coordinates of valence angle bending for groups that are on the σ(xz) plane of the $Cr_2(O_2CH)_4(H_2O)_2$ complex.

The calculations were made with the aid of molecular dimensions shown in Table 5 After several iterations a satisfactory set of force constants, listed in Table 6, 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 quite satisfactory. The potential energy distribution (PED) in each normal vibration was calculated with respect to each independent internal coordinate in order to make theoretical band assignments and to determine the mixing ratio of various modes in each band (Nakamoto and Martell, 1960)

RESULTS AND DISCUSSION

In Table 1 the frequencies of the $Cr_2(O_2CH)_4(H_2O)_2$ infrared absorptions (*Uzairu et al.*, 2003), which were assigned to its normal vibrations, are listed. However, since all the 24 atoms of the complex lie on the two planes,σ(xz) and σ(yz), of the molecule (Cotton and Rice, 1978) (also see Figures 1 - 3), 28 of the in-plane normal vibrations, made up of $15A_1(S_1 - S_{15}) + 13B_2$, belong to the groups that lie on the σ(yz) molecular plane while the remaining 15, made up of $8A_1(S_{16} - S_{23}) + 7B_1$, belong to those on σ(xz) plane This indicates that the asymmetric in-plane vibrations of the two molecular planes have different characters (B_1 and B_2) They are, therefore, orthogonal and not expected to mix But the symmetric in-plane vibrations of both molecular planes belong to the same representation (A_1), implying that they are not necessarily orthogonal and, may, therefore, couple with one another Thus, in order to facilitate the identification of the location of a normal mode in a coupled vibration for A_1 species, the labels I (for those belonging to σ(yz) plane) and II (for those on σ(xz) plane) have been added to the individual modes in Table 1

The bands at about 2855 and 2871 cm^{-1} are, respectively, ν_s(C-H) and ν_{as}(C-H) stretching modes. Splitting between them is rather small and both are doubly degenerate accidentall

Table 5. The geometrical data of $Cr_2(O_2CH)_4(H_2O)_2$ complex.

Parameter	Observed[*]	Used in this calculations
A. Valence angles (degrees)		
$\alpha_1, \alpha_3 ; \alpha_2, \alpha_4$	87.6, 88.1; 88.3, 87.6	87.85; 87.95
$\delta_1, \delta_3 ; \delta_2, \delta_4$	119.9, 19.8; 118.6, 120.0	119.85; 119.30
$\varepsilon_1 ; \varepsilon_2$	125.3 ; 124.4	124.85; 124.85
$\beta_1, \beta_3 ; \beta_2, \beta_4$	-	117.58; 117.58^a
$\phi_1, \phi_3 ; \phi_2, \phi_4$	95.7, 96.0; 88.7, 88.1	95.85; 88.4
$\eta_1, \eta_3 ; \eta_2, \eta_4$	-	127.75; 127.75^a
$\Omega_1 ; \Omega_2$	-	104.40; 104.40^b
$\alpha'_1, \alpha'_3 ; \alpha'_2, \alpha'_4$	87.6, 88.3; 88.1, 87.6	87.95; 87.85
$\delta'_1, \delta'_3 ; \delta'_2, \delta'_4$	120.0, 118.6; 119.8, 119.9	119.30; 119.85
$\varepsilon'_1 ; \varepsilon'_2$	124.4; 125.3	124.85; 124.85
$\beta'_1, \beta'_3 ; \beta'_2, \beta'_4$	-	117.58; 117.58^a
$\phi'_1, \phi'_3 ; \phi'_2, \phi'_4$	96.0, 95.7; 88.1, 88.7	95.85; 88.40
Angles between planes at Cr-Cr	88.7, 90.8; 89.7, 90.6	90.00; 90.00
OCrO angles at Cr atoms	179.5; 180.3	180.00; 180.00
B. Bond distances (Å)		
$D_1 ; D_2$	-	1.08; 1.08^b
$r_1, r_3 ; r_2, r_4$	2.009, 2.006; 2.026, 2.017	2.008; 2.022
$d_1, d_3 ; d_2, d_4$	1.263, 1.264; 1.252, 1.249	1.264; 1.250
R	2.373	2.373
$h_1 ; h_2$	2.268; 2.268	2.268; 2.268
$b_1, b_3 ; b_2, b_4$	-	0.96; 0.96^b
$D'_1 ; D'_2$	-	1.08; 1.08^b
$r_1, r_3 ; r_2, r_4$	2.017, 2.026; 2.006, 2.009	2.022; 2.008
$d_1, d_3 ; d_2, d_4$	1.249, 1.252; 1.264, 1.263	1.250; 1.264

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[a] Determined from the geometry of the complex using the values of other valence angles.

[b] Taken from (Ladd, 1999).

[*] Cotton and Rice (1978)

Table 6. Force constants of the $Cr_2(O_2CH)_4(H_2O)_2$ complex (x 10^5 dyne cm^{-1})

A. Diagonal force constants

	Coordinate	Value
1.	υ_s(C-H)	4.464296
2.	υ_s(COO)	10.956020
3.	υ_s' (COO)	6.520702
4.	υ_s(OCrO)	2.747360
5.	υ(Cr-Cr)	4.406622
6.	υ(Cr-O)	2.566425
7.	υ_s(O-H)	6.336049
8.	δ_s(ring)	0.379208
9.	δ(O-H)	0.923559
10.	r_s(C-H)	0.403914
11.	δ_s' (ring)	0.620866
12.	υ_{as}(C-H)	4.513306
13.	υ_{as}(COO)	7.633842
14.	υ_{as}(OCrO)	2.374062
15.	r_{as}(C-H)	0.411939
16.	δ_{as}(ring)	0.421494
17.	δ_{as}' (ring)	0.958778
18.	υ_{as}(O-H)	6.369861
19.	r(H_2O)	0.021278
20.	r(Cr-O)	0.041765

B. Interaction force constants

	Coordinates		Value
21.	υ_s(C-H)	r_s(C-H)	0.087452
22.	υ_s(COO)	υ_s' (COO)	0.128367
23.		υ_s(OCrO)	0.027186
24.		δ_s(ring)	0.058642
25.		δ_s' (ring)	0.003647
26.	υ_s' (COO)	υ_s(OCrO)	0.020584
27.		δ_s(ring)	0.049651
28.		δ_s' (ring)	0.003098
29.	υ_s(OCrO)	δ_s(ring)	0.004312
30.		δ_s' (ring)	0.072235
31.	υ(Cr-Cr)	δ_s(ring)	-0.127452
32.		δ_s' (ring)	-0.120371
33.	υ_s(O-H)	δ(O-H)	0. 206289
34.	δ_s(ring)	δ_s' (ring)	-0.005372
35.		δ_s(ring)	-0.003681
36.	υ_{as}(C-H)	r_{as}(C-H)	0.057298
37.	υ_{as}(COO)	υ_{as}(OCrO)	0.024621
38.		δ_{as}(ring)	0.027519
39.		δ_{as}' (ring)	0.162735
40.	υ_{as}(OCrO)	δ_{as}(ring)	0.043754
41.		δ_{as}' (ring)	0.033062
42.	δ_{as}(ring)	δ_{as}' (ring)	0.019402
43.	υ_{as}(O-H)	r(H_2O)	0.310051

The band at 1351 cm^{-1} represents the frequencies of the pure υ_s(COO) I and υ_s(COO) II identical vibrations of the two molecular planes (S_2 and S_{17}). The remaining bands due to the stretching motions of the COO groups, according to the calculations, occurred at 1463 and 1583 cm^{-1}. These are, respectively, the frequencies of υ_s'(COO) I (65) coupled with υ_s'(COO) II (35) and υ_s'(COO) II (65) coupled with υ_s'(COO) I (35), and υ_{as}(COO) I and υ_{as}(COO) II pairs of accidentally degenerate vibrations.

Tables 2 - 4 indicate that the 4 OCrO bridging groups in the complex possess a total of 8 in-plane vibrations, made up of 4 symmetric and 4 asymmetric stretching motions. The symmetric modes of the OCrO groups are assignable to the bands at 540 and 547 cm^{-1}. The band at 540 cm^{-1} is due to triply accidental degenerate vibrations. These are υ_s(OCrO) I (87) coupled with υ(Cr-Cr) I (9) and υ_s(OCrO) II (4), υ_s(OCrO) II (100) and υ_s(OCrO) II (89) coupled with υ_s(OCrO) I (6) and υ_s(Cr-Cr) I (4). However, the 547 cm^{-1} band represents the frequency of υ_s(OCrO) I (55) coupled with υ(Cr-Cr) I (41) and δ_s'(ring) I (3) modes. The 4 asymmetric OCrO stretching vibrations are also described by only two bands. The positions of these bands are located at 640 and 813 cm^{-1}, and are due, respectively, to υ_{as}(OCrO) II (S_{44}(98) + S_{45}(2)), υ_{as}(OCrO) II (S_{45}(98) + S_{44}(2)) and υ_{as}(OCrO) I (S_{57}(100)) triply degenerate modes, and υ_{as}(OCrO) I (S_{56}(100)) non-degenerate mode.

The angular vibrations of the 4 COO groups in the complex (since they are part of the rings formed by bridging the 4 HCOO$^-$ ligands to the Cr_2^{4+} central moiety) lead to the deformation of the rings. The angular vibrations that result into the ring deformations are the COO scissoring and rocking motions. In fact, the calculations show that the bands at 654, 670, 722 and 767 cm^{-1} are due to COO scissoring type ring deformation oscillations while those due to rocking type are located at about 450, 464 and 525 cm^{-1}. Apart from the band at 450 cm^{-1}, which is due to δ_{as}'(ring) II (S_{48}(99)) and δ_{as}'(ring) I (S_{66}(99)) accidentally degenerate vibrations, all the other 6 bands represent the frequencies of mixed non-degenerate ring deformations (Table 1).

The pair of terminal H atoms attached to the rings per plane (Figures 3) [illegible] also exhibit rocking vibrations. The rocking motions of the pair of H atoms on the σ(yz) plane, r_s(C-H) coupled with υ_s(COO) mode and r_{as}(C-H), have higher frequencies, 1379 and 1393 cm^{-1}, respectively, than those on the σ(xz) plane, r_s(C-H) and r_{as}(C-H) coupled with δ_{as}'(ring). The bands of the latter are, respectively, located at about 1010 and 1031 cm^{-1}.

8 and 4 normal modes, respectively, come from the pairs of H_2O ligands and Cr-O axial bonds, constituting up to about 18% of the number of vibrations of the complex. Bands for 9 of these 12 vibrations, 876, 1133, 1748, 3375, 3393 and 3401 cm^{-1} due to the H_2O ligands and 596 cm^{-1} only due to the Cr-O axial bonds, were observed. However, bands at 596 and 3375 cm^{-1} represent the frequencies of a pair of degenerate vibrations each. The remaining 3 bands predicted to be located at 113, 129 [due to r(Cr-O) (S_{63}(49) + S_{64}(23)) coupled with δ_{as}'(ring) (S_{66}(28)) and r(Cr-O) (S_{64}(66) + S_{63}(32)) coupled with δ_{as}'(ring) (S_{66}(2)) modes, respectively] and 4655 cm^{-1} [due to δ (O-H) (S_{12}(99)) coupled with υ_s(O-H) (S_9(1))] were not observed in our measurements.

Of all the many bands due to the in-plane vibrations of the complex, the Cr-Cr stretching band is of particular interest since it represents the frequency of vibration of the nucleus of the complex. Thus it is understandable that 7 other normal modes of the complex, υ_4(41%), υ_5(9%), υ_{11}(4%), υ_{15}(26%), υ_{20}(4%), υ_{21}(1%) and υ_{23}(11%), are sensitive to it, where the percentages in the parentheses indicate the contributions of the υ(Cr-Cr) stretching mode to the various vibrations. The band at 538 cm^{-1} (υ_6) is the only one due mainly to υ(Cr-Cr), making about 68% of the vibration, coupled simultaneously with the symmetric stretching modes of all the 4 OCrO bridging groups of the two molecular planes.

The observed frequencies were satisfactorily reproduced by the final force field listed in Table 6. The fit for groups in the $Cr_2(O_2CH)_4(H_2O)_2$ complex is of the same quality as those obtained for the same groups in CH_3COO^- ion (Uzairu and Harrison, 2005), H_2O_2 (Arnau and Giguère, 1974), $Cr_2(mhp)_4$ complex (Cotton and Walton, 1993) and Cr($acac$)$_2$ (Nakamoto and Martell, 1960). In Table 7, the force constants of various groups in the CH_3COO^- ion, H_2O_2, $Cr_2(mhp)_4$ and $Cr(acac)_2$ are

Table 7. Force constants (x 10^5 dyne cm^{-1}) for some groups in the $Cr_2(O_2CH)_4(H_2O)_2$ complex compared with values known for closer molecules/fragments

Coordinate(s)	Value				
	Cr($acac$)[a]	CH_3COO^- ion[b]	H_2O_2[c]	$Cr_2(mhp)_4$[d]	$Cr_2(O_2CH)_4(H_2O)_2$
υ_s(C-H)		4.848564			4.464296
υ_s(COO)		11.968535			10.956020
υ_s(OCrO)	2.400836				2.747360
υ(Cr-Cr)				4.73	4.406622
δ_s(ring)	0.110454				0.379208
υ_s(O-H)			5.669		6.336049
δ_s'(ring)	0.605610				0.620866
δ(O-H)			0.900		0.923559
r_s(C-H)		0.387420			0.403914
(ring)	0.414295				0.421494
COO)		7.581072			7.633842
υ_{as}(OCrO)	2.345836				2.374062
(C-H)		0.394464			0.411939
(O-H)			5.380		6.369861
υ_{as}(C-H) r_{as}(C-H)		0.057687			0.057298

Nakamoto and Martell 1960), [b] Uzairu and Harrison (2006), [c] Arnau and Giguère (1974); [d] Cotton and Walton (1993) listed Comparing the values given in this table, it is seen that agreement between the force constants of the groups in these molecules and the complex under study is very good This agreement shows that the transfer of the force constants of some groups in these molecules to $Cr_2(O_2CH)_4(H_2O)_2$ was quite reasonable

REFERENCES

Arnau, J. L. and Giguére, P A., 1974. Vibrational Spectra and Normal Coordinate Analysis of Crystalline H_2O_2, D_2O_2 and HDO_2, *Spectrochim. Acta*, 30A, 777

Bratton, W K., Cotton, F A, Debeau, M and Walton, R A, 1971 Vibrational Studies of Dinuclear Compounds Containing Quadruple Bonded Pairs of Molybdenum and Rhenium Atoms, *J Coord Chem*, 1 121

Clark, R. J. H. and Ferris, L. T H., 1981 Resonance Raman, Excitation Profile and Electronic Structural Studies of $Ru_2(O_2CR)_4L_2$ Complexes, *Inorg. Chem.*, 20 2759.

Clark, R. J. H., Hempleman, A J. and Tocher, D. A., 1988*a*. Infrared, Raman and Resonance Raman and Excitation Profile Studies of Os_2 $(O_2CCH_3)_4Cl_2$ and $Os_2(O_2CCD_3)_4Cl_2$. The Assignment of the Os-Os Stretching Vibration for a Complex Involving Osmium-Osmium Multiple Bond, *J Am Chem. Soc.*, 5968.

Clark, R. J. H., Hempleman, A J and Kurmoo, M, 1988*b* Infrared, Raman and Resonance Raman Spectra of Tetraacetato Dimolybdenum and Its Deuterated Analog, *J. Chem. Soc., Dalton Trans*, 793.

Clark, R. J. H. and Hempleman, A. J., 1989. Infrared. Raman and Resonance Raman and Excitation Profile Studies of $Rh_2(O_2CCH_3)_4L_2$ (L = $AsPH_3$, $SbPH_3$), *Inorg Chem*, **28:** 746

Clark, R. J. H., West, D. J. and Withnall, R W., 1992 Electronic, Infrared, Raman and Resonance Raman Spectra of the Dirhodium Tetrakis (Thiocarboxylate) Complexes $Rh_2(OSCCH_3)_4L_2$ (L = PPH_3, $AsPH_3$, CH_3COSH), *Inorg. Chem.*, **31**: 456.

Cotton, F. A. and Norman, Jr., J. G., 1972. Molybdenum (II) Triflouroacetate Dimer, *J. Am. Chem Soc*, **94** 5697

Cotton, F. A. and Rice, G. W., 1978. Crystal and Molecular Structure of Tris[Tetra-μ- Formato Dichromium (II)] Decahydrate: A Case of Unusually Good False Minimum in a Structure Solution, *Inorg. Chem.*, **17** 688.

Cotton, F. A. and Walton, R. A., 1993. Multiple Bonds between Metal Atoms, 2nd Edit., Clarendon Press, Oxfrod, p. 735.

Garner, C. D., Senior, R G and King, T J., 1976. Preparation and Characterization of Chromium (II)-Molybdenum (II) Tetraacetate. A Compound Containing a Heteronuclear Quadruple Metal-Metal Bond, *J. Am. Chem. Soc.*, **98**: 647

Hollenstein, H., R. Schar, R. W., Schwizgebel, N., Grassi, G. and Günthard, Hs. H., 1983. A Transferable Valence Force Field for Polyatomic Molecules. A Scheme for Glycolic Acid and Methyl Glycolate, *Spectrochim. Acta*, **39A**, 193.

Hutchinson, B., Morgan, J., Cooper, III, C B., Mathey, Y and Shriver, D. F., 1979. Metal Isotopic Shifts in the Raman Spectrum of $Mo_2(O_2CCH_3)_4$, *Inorg. Chem.*, **18:** 2048

Ketteringham, A. P., Oldham, C and Peacock, C J, 1976 *Raman Spectra of Multiple Bonded Metal Species, J Chem Soc, Dalton Trans*, pp1640

Ladd, M., 1999 Introduction to Physical Chemistry, 3rd Edit., *Cambridge University Press, UK*, p 251

Martin, D. S., Newman, R A and Fanwick, P E., 1982 Polarized Electronic Absorption Spectra of Tetrakis (μ-Triflouroacetato) Dimolybdenum (II), and Tetrakis (μ-Triflouroacetato) Bispyridine Dimolybdenum (II), *Inorg. Chem*, **21** 3400.

Miskowski, V M, Dallinger, R F, Christoph, C G, Morris, D E., Spies, G H and Woodruff, W H, 1987 Electronic, Infrared, Raman and Resonance Raman Spectra of Dirhodium Tetracarboxylate Complexes *Inor Chem.*, 26. 2127

Nakamoto, K & Martell, A. E., 1960. Infrared Sp ectra of Metal Chelate Compounds I A Normal Coordinate Treatment on Bis (Acetylacetonato)-Cu(II), *J. Chem Phys.*, 32: 588

Oldham, C., Davies, J. E D and Ketteringham, A P., 1971 Low Frequency Vibration Spectra of Some Rhenium (III) Dimeric Complexes, *J Chem Soc., Chem Commun.*, pp 572

Santure, D. J, Huffman, J C and Sattelberger, A P, 1985 Synthesis and Properies of Ditungsten (II) Tetracarboxylates, *Inorg Chem*. **24**: 37

Uzairu, A., Harrison, G F. S and Adamu, A. 2003. The Infrared Spectrum of Diaquo Tetra-μ-Formato Dichromium (II): A Normal Coordinate Treatment on 1 1 Formato Complex. *Global J Pure & Appl Sci*, 9 (1) 81

Uzairu, A., Harrison, G F S. and Adamu, A., 2004*a* Normal Coordinate Treatment on The Diaquo Tetra-μ-Formato Dichromium (II) Complex in the Solid State I. Calculation of the 66 Genuine Symmetry Coordinates of the Complex and Their Assignments to Vibrational Modes. *J. Chem. Soc.* (Nig.), **29(2)**: 128

Uzairu, A., Harrison, G F S and Adamu, A 2004*b* Normal Coordinate Treatment on The Diaquo Tetra-μ-Formato Dichromium (II) Complex in the Solid State II Infrared Spectral Band Assignments of the Out-of-Plane Vibrations of he Complex, *J. Chem Soc* (Nig), **29**(2). 134.

Uzairu, A. and Harrison, G. F S., 2005. A Recalculation of the Normal Vibrations of the Acetate Anion, *J.Chem.Soc.*(Nig), **30(2)** 119

Woodward, L. A., 1972. Introduction to the Theory of Molecular Vibrations and Vibrational Spectroscopy, Oxford University Press, pp 5 237