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Calculations of the 102 genuine internal coordinates of diaquo tetra-μ-acetato dichromium (II) complex and their assignments to vibrational modes

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ABSTRACT

The calculations of the 102 genuine internal coordinates of diaquo tetra-μ-acetato dichromium (II) complex and their assignments to vibrational modes have been done. The results showed that the 102 normal modes of the complex were partitioned into $28\mathbf{A_g} + 29\mathbf{B_u}$ in-plane and $23\mathbf{B_g} + 22\mathbf{A_u}$ out-of-plane vibrations, carried out by 9 characteristic groups in the form of stretching, deformation, rocking and torsion motions. The breakdown of the different types and forms of the vibrational modes of the complex as well as the number of normal modes possessed by the characteristic groups and the activity of each of these in infrared or Raman are presented.

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INTRODUCTION

Recently, we reported the normal coordinate analyses and band assignments of the infrared spectrum of diaquo tetra-μ-formato dichromium (II) complex [1-4]. Bands for symmetric stretching vibrations of Cr-Cr and bridging Cr-O bonds, which are of great importance in assigning electronic absorption bands of the $Cr_2(O_2CR)_4L_2$ complexes, were assigned theoretically for the first time. The studies showed that the symmetric bridging Cr-O normal modes couple with υ(Cr-Cr) and δ_s'(Ring) vibrational modes and were assigned to 540 and 547 cm^{-1} bands. Furthermore, the band for Cr-Cr stretching was inferred to occur in the same region as the symmetric bridging Cr-O stretching modes, 538 cm^{-1}, and mixes with υ_s(OCrO) (32%).

However, it has been experimentally observed that both Cr-Cr and bridging Cr-O distances in $Cr_2(O_2CR)_4L_2$ compounds depend on the nature of the R group [5]. It is evident, therefore, that the frequencies of Cr-Cr and bridging Cr-O stretching modes would be sensitive to the mass as well as inductive character of the R group. Thus it is desirable to obtain the vibrational spectra of these compounds with R = CH_3, C_2H_5, etc. below 650 cm^{-1} where the Cr-Cr and some of the bridging Cr-O modes may appear. In addition, normal coordinate treatments must be carried out to make theoretical assignments, especially on Cr-Cr and bridging Cr-O bands as well as to see coupling between various vibrational modes.

As for diaquo tetra-μ-acetato dichromium (II) complex, $Cr_2(O_2CCH_3)_4(H_2O)_2$, previous infrared spectral investigations were concerned only with the ligand vibrations [6,7], and no direct information is as yet available on its Cr-Cr and the bridging Cr-O vibrations. We have obtained the infrared spectrum of the diaquo tetra-μ-acetato dichromium (II) complex in the range 4000 and 400 cm^{-1} and made normal coordinate treatments for the purpose mentioned above. However, because of the very large size of the $Cr_2(O_2CCH_3)_4(H_2O)_2$ complex, the report was partitioned into three parts. In the present paper, 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 are presented. In subsequent parts, results of the calculations of the in-plane and out-of-plane vibration frequencies and the comparison of these with observed ones, potential energy distributions and theoretical band assignments for the infrared active modes of the complex will be reported.

CALCULATIONS

The crystal structure of the diaquo tetra-μ-acetato dichromium (II) complex was reported by Cotton and co-workers [8]. According to that study, each unit cell of the complex has 4 crystallographically equivalent $Cr_2(O_2CCH_3)_4(H_2O)_2$ molecular units with $\mathbf{C_{2h}}$ site

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symmetry. Thus normal coordinate treatments on a $\mathbf{C_{2h}}$ $Cr_2(O_2CCH_3)_4(H_2O)_2$ molecule are required in principle to interpret the solid state infrared spectrum of the complex.

The 102 genuine normal modes of the $\mathbf{C_{2h}}$ $Cr_2(O_2CCH_3)_4(H_2O)_2$ molecule are subdivided into $28\mathbf{A_g}$ + $23\mathbf{B_g}$ + $29\mathbf{B_u}$ + $22\mathbf{A_u}$ classes. The bond lengths, valence and bond bending angles of the molecule, whose increments are the elementary internal coordinates, are shown in Figs. 1 – 4. Because of the large size and structure of the $Cr_2(O_2CCH_3)_4(H_2O)_2$ molecule, there are a total of 144 elementary internal coordinates, thus introducing 42 redundant ones. The breakdown of the species spanned by the 144 and 42 internal and redundant coordinates, respectively, is shown in Table 1. The classification of representations as in-plane and out-of-plane with respect to the plane of the molecule as well as the identification of their activity in infrared or Raman are also given in the table.

Finally, employing symmetry considerations and the 144 elementary internal coordinates as basis [9], the 102 genuine internal coordinates were calculated for the $Cr_2(O_2CCH_3)_4(H_2O)_2$ molecule. The 102 internal coordinates obtained and the assignment of each one of them to a vibrational mode are presented in Tables 2 – 5. However, the 42 redundant internal coordinates have no physical significance and, therefore, need not be reported.

Table 1. Showing the number of individual species in the Cartesian basis, genuine modes, internal basis and redundant coordinates of the $Cr_2(O_2CCH_3)_4(H_2O)_2$ complex

Species	N_C	$N_{R\,\&\,T}$	N_{C-6}	N_{int}	N_{redund}	Type	Activity
$\mathbf{A_g}$	29	1	28	44	16	in-plane	Raman
$\mathbf{B_g}$	25	2	23	28	5	out-of-plane	Raman
$\mathbf{A_u}$	23	1	22	29	7	out-of-plane	Infrared
$\mathbf{B_u}$	31	2	29	43	14	in-plane	Infrared

RESULTS AND DISCUSSION

Tables 2 - 5 contain the description of all the 102 genuine normal modes of vibration of the $Cr_2(O_2CCH_3)_4(H_2O)_2$ molecule as obtained from the results of the calculations. These also indicate that, of the 102 vibrations, $28\mathbf{A_g}$ + $29\mathbf{B_u}$ are in-plane and are separable from $23\mathbf{B_g}$ + $22\mathbf{A_u}$ out-of-plane vibrations. As may similarly be seen from the tables, all the symmetric normal vibrations are in-plane and are made up of only stretching, deformation and rocking motions of different groups. On the other hand, the out-of-plane vibrations of the complex include some twisting and wagging (out-of-plane rocking) modes. However, coupling between in-plane and out-of-plane vibrations is not expected since they belong to different representations.

To distinguish between the vibrations of the two types of Cr-O bonds in the molecule, use has been made of OCrO to represent bridging Cr-O bonds and just Cr-O for axial Cr-O bonds. Thus υ_s(OCrO) represents symmetric stretching mode of bridging Cr-O bonds whereas υ_s(Cr-O) that of axial Cr-O bonds, etc.. Also, the bridging of the four CH_3COO^- ligands to the Cr_2^{4+} central moiety results in the formation of four 5-membered rings. The deformation vibrations of these rings were denoted δ(Ring) in the tables, with or without prime(s) to differentiate between types.

The results of the calculations further indicate the 36 atoms of the molecule to be subdivided into 9 characteristic groups during vibration and that, as may be seen from Tables 2 – 5, all the 102 normal vibrations are carried out by them. However, some of these distinct groups are in multiples. In addition, these characteristic groups exhibited only four distinct types of vibrations – namely stretching, deformation, rocking and torsion vibrations. The breakdown of the different types and forms of the vibrational modes of the $\mathbf{C_{2h}}$ $Cr_2(O_2CCH_3)_4(H_2O)_2$ molecule is given in Table 6, which shows 21 kinds.

Finally, the number of vibrations possessed by each characteristic group, the representations spanned by the vibrations of the groups, the multiplicity of the groups in the $Cr_2(O_2CCH_3)_4(H_2O)_2$ molecule and the

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Table 6: The breakdown of groups in the complex and the type and number of normal modes they possess

Group	υ	υ_s	υ_s'	υ_s''	υ_s'''	υ_{as}	υ_{as}'	δ_s	δ_s'	δ_s''	δ_s'''	δ_{as}	δ_{as}'	r_s	r_s'	r_{as}	r_{as}'	π	τ_{as}	τ_{as}'	τ_{as}''	Total per group
CH_3	-	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	-	-	-	-	32
C-C	-	2	2	-	-	-	-	-	-	-	-	-	-	2	2	2	2	-	-	-	-	12
COO	-	2	2	-	-	2	2	-	-	-	-	-	-	2	2	-	-	-	-	-	-	12
OCrO	-	2	2	-	-	2	2	2	-	-	-	2	-	2	-	2	-	-	-	-	-	16
Cr-Cr	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1	-	-	-	2
Cr-O	-	1	-	-	-	1	-	-	-	-	-	-	-	1	-	1	-	-	-	-	-	4
H_2O	-	1	1	-	-	1	1	1	-	-	-	-	1	1	1	1	-	-	1	-	-	10
Ring	-	-	-	-	-	-	-	2	2	-	-	2	2	-	-	-	-	-	-	-	-	8
CH_3COO	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2	2	2	6
Total	1	10	9	2	2	8	7	7	4	2	2	6	5	10	7	8	4	1	3	2	2	102

Table 7: The structure of normal modes as per the class and activity of the vibrations for each group in the complex

Group	CH_3	C-C	COO	OCrO	Cr-Cr	Cr-O	H_2O	Ring	CH_3COO	Total
Multiplicity	4	4	4	4	1	2	2	4	4	
No. of infrared active normal modes and species spanned	16 $6\mathbf{A_u} + 10\mathbf{B_u}$	6 $2\mathbf{A_u} + 4\mathbf{B_u}$	6 $2\mathbf{A_u} + 4\mathbf{B_u}$	8 $4\mathbf{A_u} + 4\mathbf{B_u}$	1 $\mathbf{B_u}$	2 $\mathbf{A_u} + \mathbf{B_u}$	6 $3\mathbf{A_u} + 3\mathbf{B_u}$	4 $2\mathbf{A_u} + 2\mathbf{B_u}$	2 $2\mathbf{A_u}$	51 $22\mathbf{A_u} + 29\mathbf{B_u}$
No. of Raman active normal modes and species spanned	16 $10\mathbf{A_g} + 6\mathbf{B_g}$	6 $4\mathbf{A_g} + 2\mathbf{B_g}$	6 $4\mathbf{A_g} + 2\mathbf{B_g}$	8 $4\mathbf{A_g} + 4\mathbf{B_g}$	1 $\mathbf{A_g}$	2 $\mathbf{A_g} + \mathbf{B_g}$	4 $2\mathbf{A_g} + 2\mathbf{B_g}$	4 $2\mathbf{A_g} + 2\mathbf{B_g}$	4 $4\mathbf{B_g}$	51 $28\mathbf{A_g} + 23\mathbf{B_g}$
Total number of normal modes and species spanned	32 $10\mathbf{A_g} + 6\mathbf{B_g}$ + $6\mathbf{A_u} + 10\mathbf{B_u}$	12 $4\mathbf{A_g} + 2\mathbf{B_g}$ + $2\mathbf{A_u} + 4\mathbf{B_u}$	12 $4\mathbf{A_g} + 2\mathbf{B_g}$ + $2\mathbf{A_u} + 4\mathbf{B_u}$	16 $4\mathbf{A_g} + 4\mathbf{B_g}$ + $4\mathbf{A_u} + 4\mathbf{B_u}$	2 $\mathbf{A_g} + \mathbf{B_u}$	4 $\mathbf{A_u} + \mathbf{B_u}$ + $\mathbf{A_g} + \mathbf{B_g}$	10 $2\mathbf{A_g} + 2\mathbf{B_g}$ + $3\mathbf{A_u} + 3\mathbf{B_u}$	8 $2\mathbf{A_g} + 2\mathbf{B_g}$ + $2\mathbf{A_u} + 2\mathbf{B_u}$	6 $2\mathbf{A_u} + 4\mathbf{B_g}$	102 $28\mathbf{A_g} + 23\mathbf{B_g}$ + $22\mathbf{A_u} + 29\mathbf{B_u}$

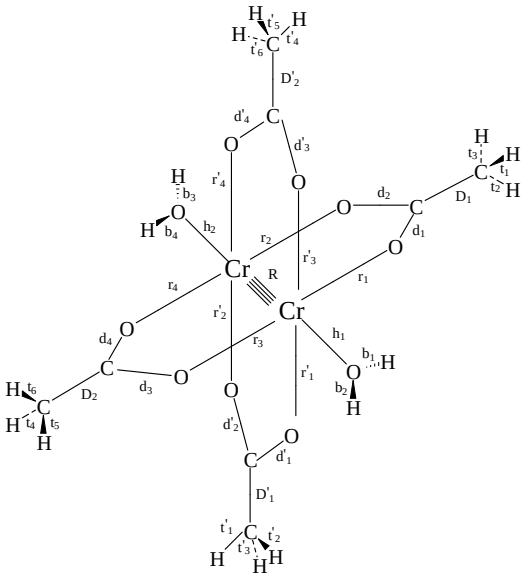


Fig. 1. Elementary stretching internal coordinates of the molecule

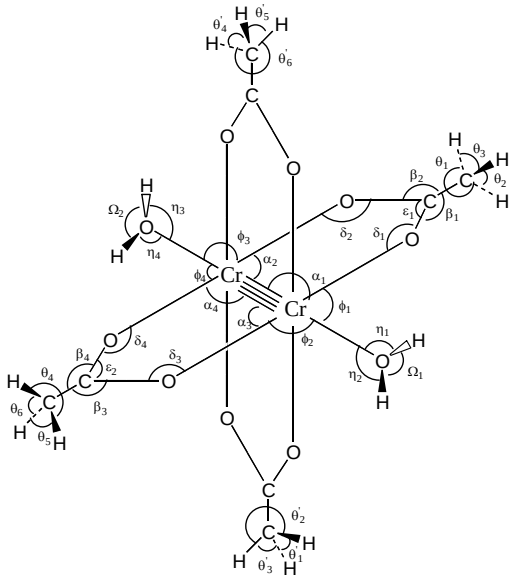


Fig. 2: Some of the elementary valence angle internal coordinates of the molecule

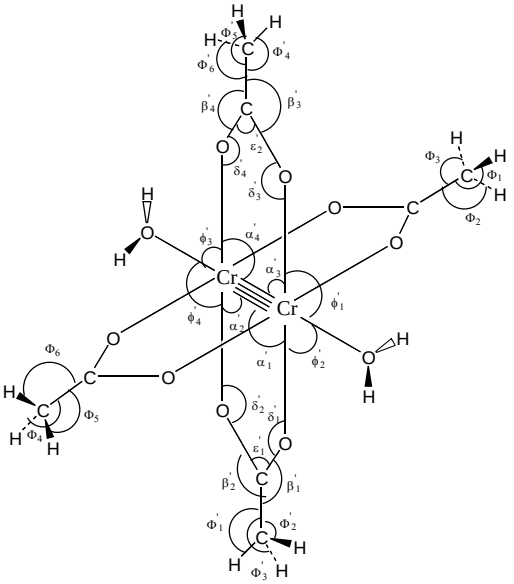


Fig.3: The remaining elementary valence angle internal coordinates of the molecule

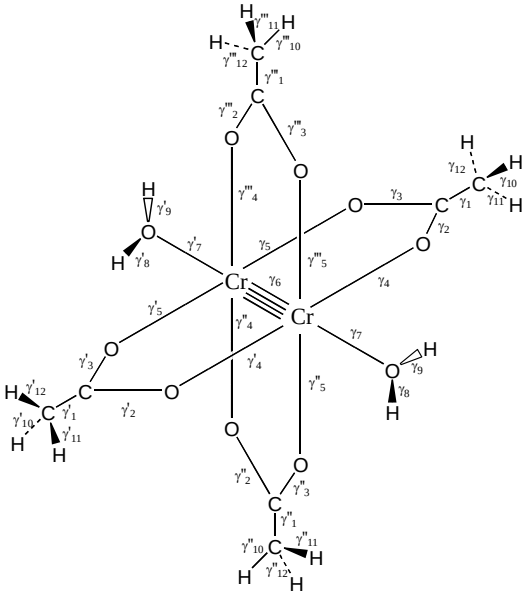


Fig. 4: Elementary bond bending angle internal coordinates of the molecule

number of modes for each group that are active in infrared or Raman are presented in Table 7. On the whole, there are 51 normal modes that are infrared and Raman active each and no normal vibration is both infrared and Raman active in the molecule.

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