Acta Cryst. (1986). B**42**, 529–533

X-ray Crystallographic Study of Tetragonal and Monoclinic β_1-V_2H

By Yasutoshi Noda and Katashi Masumoto

Department of Materials Science, Faculty of Engineering, Tohoku University, Aramaki Aoba, Sendai 980, *Japan*

Shigetoshi Koike

Department of Physics, Science University of Tokyo, Kagurazaka 1-3, *Shinjuku-ku, Tokyo* 162, *Japan*

Taira Suzuki

Department of Applied Physics, Science University of Tokyo, Kagurazaka 1-3, *Shinjuku-ku, Tokyo* 162, *Japan*

and Shoichi Sato

Institute for Solid State Physics, University of Tokyo, Roppongi 7-2-1, *Minato-ku, Tokyo* 106, *Japan*

(*Received* 21 *August* 1985; *accepted* 14 *March* 1986)

Abstract

Tetragonal β_1-V_2H: $M_r = 102{\cdot}9$, $I4_1/amd$, $a = 6{\cdot}0012\,(3)$, $c = 6{\cdot}6188\,(9)$ Å, $V = 238{\cdot}37\,(8)$ Å^3, $Z = 8$, $D_x = 5{\cdot}73$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}7107$ Å, $\mu = 143{\cdot}3$ mm^{-1}, $F(000) = 376{\cdot}0$, room temperature, final $R = 0{\cdot}049$ for 456 independent reflections; monoclinic β_1-V_2H: $M_r = 102{\cdot}9$, Cm, $a = 4{\cdot}4566\,(5)$, $b = 3{\cdot}0022\,(2)$, $c = 4{\cdot}4760\,(5)$ Å, $\beta = 95{\cdot}609\,(8)^\circ$, $V = 59{\cdot}60\,(1)$ Å^3, $Z = 2$, $D_x = 5{\cdot}73$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}7107$ Å, $\mu = 143{\cdot}3$ mm^{-1}, $F(000) = 94{\cdot}0$, room temperature, final $R = 0{\cdot}080$ for 672 independent reflections. The structure of β_1-V_2H crystals depends upon the conditions of growth: if grown under tensile stress, the structure is tetragonal while if grown without applied stress it is monoclinic. The crystal structures have been studied using a four-circle diffractometer with Mo $K\alpha$ radiation and were refined by the method of full-matrix least squares. The crystal data and atomic parameters of the fundamental body-centered cell formed by the V atoms are very close in the two structures except for an axial angle. It is pointed out that the crystal data for tetragonal β_1-V_2H depend on the magnitude of the tensile stress applied during crystal growth.

Introduction

Vanadium hydride (β_1-V_2H) has been regarded as monoclinic (space group Cm) on the basis of electron, X-ray and neutron diffraction studies (Takano & Suzuki, 1974; Asano, Abe & Hirabayashi, 1976; Koike & Suzuki, 1981; Moss, 1983). Besides Cm, the space groups $C2$ and $C2/m$ were also proposed (Wanagel, Sass & Batterman, 1972). On the other hand, recent X-ray and neutron diffraction studies indicated that the arrangement of hydrogen atoms belongs to that of the tetragonal system ($I4_1/amd$) (Noda, Kajitani, Hirabayashi & Sato, 1985; Kajitani & Hirabayashi, 1985*a*). The tetragonal and monoclinic structure models proposed are shown in Fig. 1: H atoms occupy orderly specific interstices in the fundamental body-centered lattice of V atoms. In the case of the tetragonal model (*a*), the row of H atoms at the face-centered positions in the fundamental lattice is normal to that at the edge-centered positions, while the corresponding rows are parallel to each other in the case of the monoclinic model (*b*). The unit cell is described as $a \simeq 2a_0$ and $c \simeq 2c_0$ for the tetragonal model, and as $a \simeq c \simeq (a_0^2 + c_0^2)^{1/2}$, $b \simeq a_0$ and $\beta \simeq 95^\circ$ for the monoclinic model, where a_0 and c_0 are unit-cell dimensions of the fundamental body-centered cell. However, it is not clear which structure is the most stable for β_1-V_2H, or whether both structures are possible.

In the present study, it has been found that the tetragonal structure resulted from crystal growth under tensile stress while the monoclinic structure resulted from no stress. The crystal structures of these two types have been analyzed by X-ray diffraction. Although the atomic scattering factor of an H atom is too small to be detected easily by X-ray diffraction, the displacement of V atoms reflects the ordering of H atoms. The two structures will be compared on the basis of the crystal data of their fundamental body-centered cells.

Experimental

(1) *Sample preparation and X-ray intensity measurement*

Single crystals of V_2H were grown by solid-phase transformation from α(b.c.c.) to β_1-V_2H. The growth conditions are shown schematically in Fig. 2. The vanadium single crystals were supplied by FEI Co.

0108-7681/86/060529-05$01.50

© 1986 International Union of Crystallography

(grown by the method of electron-beam zone melting). They were cut with a wire saw. After the samples were annealed at 1800 K in ultra-high vacuum, hydrogen was charged by equilibration with the gas atmosphere at 563 K. The tetragonal structure resulted from cooling under tensile stress, while the monoclinic one resulted from the shaped end under no external stress. The shapes and dimensions of the single crystals are shown in Fig. 3. Their orientations were determined by taking Laue photographs. The tetragonal and the monoclinic crystals were then cut using a wheel and ground into spheres of 0·186 (3) and 0·178 (3) mm in diameter respectively with a piece of No. 1000 emery paper.

The unit-cell dimensions listed in Table 1 were determined by a least-squares calculation using 26 reflections in the 2θ range from 70 to 75° with the use of Mo $K\alpha_1$ radiation ($\lambda = 0{\cdot}70926$ Å).

Table 1. *Crystal data and experimental conditions for X-ray measurements of tetragonal and monoclinic* β_1-V_2H

Figures in parentheses are standard deviations from the least-squares calculation and do not represent absolute accuracy.

Crystal system	Tetragonal	Monoclinic
Space group	$I4_1/amd$	Cm
Unit-cell dimensions		
a (Å)	6·0012 (3)	4·4566 (5)
b (Å)	—	3·0022 (2)
c (Å)	6·6188 (9)	4·4760 (5)
β (°)	—	95·609 (8)
V (Å^3)	238·37 (8)	59·60 (1)
Z	8	2
D_x (g cm^{-3})	5·73	5·73
$F(000)$	376·0	94·0
μ(Mo $K\alpha$) (cm^{-1})	143·3	143·3
Temperature (K)	301	
Radiation	Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å)	
μr	1·33	1·28
Monochromator	Graphite ($2\theta_M = 12{\cdot}285°$)	
Collimator	0·5 mm diameter	
Detector aperture	1·15°	
Scan mode	ω scan ($2\theta \le 100°$) θ–2θ scan ($60° \le 2\theta < 150°$)	
Scan width (° in θ)	3·5 (ω scan) 2·0+tanθ (θ–2θ scan)	3·75 2·2+tan θ
Scan rate	2° min^{-1} in θ	
$2\theta_{\max}$ [(sin $\theta/\lambda)_{\max}$]	150° [1·359 Å^{-1}]	

Integrated intensities were measured at room tempearature using an automated four-circle diffractometer (Rigaku AFC-3) and Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). The half-width of the fundamental 101 reflection was 0·4° for both crystals, indicating that the samples were of similar quality to that in the previous study (Noda, Kajitani, Hirabayashi & Sato, 1985). Any variants which might be introduced during the transformation from α(b.c.c.) to β_1-V_2H phase in the cooling process were not observed in the diffraction pattern up to $2\theta = 150°$. The peaks trailed on both sides of the ω-scan axis owing to a strain which was possibly introduced either in the phase transformation from α to β_1 or in the preparation process of the spherical samples.

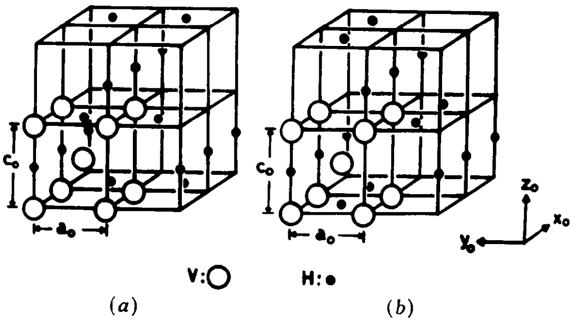


Fig. 1. Structures of β_1-V_2H. (a) Tetragonal model. (b) Monoclinic model. Vanadium atoms are drawn only for one fundamental body-centred cell of the metal lattice.

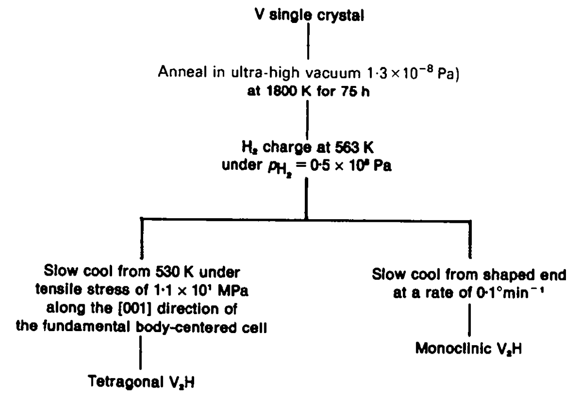


Fig. 2. Block diagram for growing tetragonal and monoclinic β_1-V_2H single crystals.

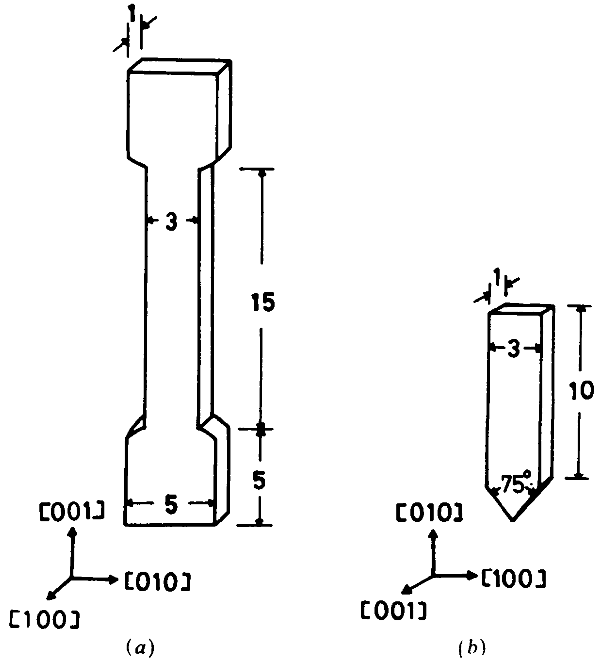


Fig. 3. Dimensions (in mm) of single crystals. (a) Tetragonal and (b) monoclinic crystals. The Miller indices are based on the fundamental body-centered cell.

The integrated intensity obtained by the ω-scan mode was greater than that obtained by the θ-2θ-scan mode and was used for the low-angle reflections. For the high-angle reflections, the θ-2θ scan mode was adopted to cover the peak splitting by the $K\alpha_1$ and $K\alpha_2$ components. In the intermediate region ($60° \leq 2\theta \leq 100°$), the reflections were measured by both scan techniques and the data of higher integrated intensity were adopted for the analysis. The experimental conditions of the intensity measurement are listed in Table 1. In all, 1371 non-zero intensities (456 independent) were obtained for tetragonal V_2H and 1283 (672) for monoclinic V_2H.

(2) *Structure refinement*

The diffraction intensity was corrected for Lorentz, polarization and absorption effects. The absorption correction was performed by the Lagrange interpolation method for spherical crystals with the transmission factor taken from *International Tables for X-ray Crystallography* (1959). The absorption correction factors for $|F_o|$'s were in the range 0·40 to 0·51.

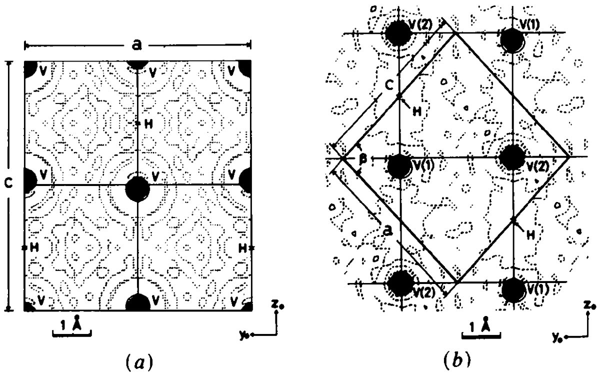
The space group $I4_1/amd$ was adopted for tetragonal V_2H following the previous study (Noda, Kajitani, Hirabayashi & Sato, 1985) in structure refinement, and Cm was confirmed for monoclinic V_2H from among Cm, $C2$ and $C2/m$ on the basis of Hamilton's test (*International Tables for X-ray Crystallography*, 1974). Parameters were refined by the full-matrix least-squares program *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979) using all the observed reflections. The function minimized was $\sum w(|F_o|-|F_c|)^2$, where $w=[\sigma(\text{counting statistics})^2+(0{\cdot}015|F_o|)^2]^{-1}$. The parameters refined were the scaling factor, positional and anisotropic thermal parameters of the V atom, and isotropic secondary-extinction parameters (Coppens & Hamilton, 1970). The parameters of the H atom were not included in the refinements, since the R value was not improved by changing these parameters. The scattering factors of the neutral V atom were taken from *International Tables for X-ray Crystallography* (1974), taking into account the anomalous-dispersion effect. The smallest extinction factor $y(=F_o^2/F_c^2)$ was 0·63 for the tetragonal and 0·78 for the monoclinic crystal. $(\Delta/\sigma)_{\max}=0{\cdot}20$ and 0·93 for the tetragonal and the monoclinic crystal, respectively.*

Results and discussion

Fig. 4 shows Fourier maps of the tetragonal and monoclinic V_2H structures in the plane $x_0=0$ of the fundamental body-centered lattice. The V atoms are displaced alternately up and down along the [001] direction of the fundamental cell. The displacements may be due to the alternate occupation of edge-centered positions by the H atoms as shown in Figs. 1(*a*) and 1(*b*), that is, the V atom tends to shift from its neighboring H atoms. Note the spherical charge distribution of the V atom in both cases; this is contrary to the large asphericity with elongation along the [001] direction found for tetragonal V_2H in the previous work, which was attributed to the static displacement of the V atom (Noda, Kajitani, Hirabayashi & Sato, 1985).

The refinement functions and final atomic parameters are listed in Tables 2 and 3, respectively. The parameters for tetragonal V_2H are based on the centrosymmetric second setting of the space group $I4_1/amd$ (*International Tables for X-ray Crystallography*, 1969). The listed positional parameters of the V atom in 16 (h) of $(0, x, z)$ deviate from those for the ideal body-centered lattice ($x=\frac{1}{2}, z=\frac{1}{4}$). The magnitude of the displacement was estimated to be 0·1133 (2) Å, in the [001] direction. In the case of monoclinic V_2H, the V atoms occupy two crystallographically independent positions. The origin of the x and z coordinates in Cm is chosen to put V (2) at $(\frac{3}{4}, 0, \frac{3}{4})$. The displacement of the V atom is estimated by taking an average between those of the V (1) and the V (2) atoms, resulting in a value of 0·1094 (5) Å along the [001] axis of the fundamental body-centered cell.

The displacements of the V atoms in tetragonal and monoclinic V_2H suggest that the ordered arrangements of H atoms correspond to those shown in Figs. 1(*a*) and 1(*b*), respectively. Direct investigation into the difference in the H-atom arrangements is left for a future neutron diffraction study. The neutron



(*a*) (*b*)

Fig. 4. Fourier maps in the plane $x_0=0$ of the fundamental body-centered lattice. (*a*) Tetragonal and (*b*) monoclinic β_1-V_2H. Contours are drawn at 20 e Å^{-3} followed by every 40 e Å^{-3}; dotted lines indicate zero level.

---

* Lists of structure factors for the tetragonal and monoclinic β_1-V_2H have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 42832 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Refinement functions for tetragonal and monoclinic* β_1-V_2H

	Tetragonal	Monoclinic
Observed reflections (n)	1371	1283
Parameters (p)	13	12
$R(F)$	0·041	0·086
$wR(F)$	0·076	0·125
S	4·04	6·72
Internal consistency between equivalent reflections	0·019	0·008
Independent reflections	456	672
$R(F)$	0·049	0·080
$wR(F)$	0·055	0·123

Table 3. *Final atomic parameters for tetragonal and monoclinic* β_1-V_2H

Tetragonal ($I4_1/amd$)		Monoclinic (Cm)	
V at 16(h):(0, x, z)		V(1) at 2(a):(x, 0, z)	
H at 8(c):(0, 0, 0)		V(2) at 2(a):(x, 0, z)	
		H at 2(a):(x, 0, z)	
(a) Positional parameters			
V	x 0·49964 (6)	V(1)	x 0·2832 (2)
	z 0·26712 (3)		z 0·2171 (2)
		V(2)	x 0·75
			z 0·75
		H	x 0·0
			z 0·5
(b) Thermal parameters (Å^2)			
V	U_{11} 0·00662 (12)	V(1)	U_{11} 0·0091 (3)
	U_{22} 0·00608 (12)		U_{22} 0·0065 (3)
	U_{33} 0·00546 (9)		U_{33} 0·0063 (3)
	U_{23} −0·00068 (7)		U_{13} 0·0006 (2)
	$U_{12}=U_{13}=0{\cdot}0$		$U_{12}=U_{23}=0{\cdot}0$
		V(2)	U_{11} 0·0041 (2)
			U_{22} 0·0047 (2)
			U_{33} 0·0045 (2)
			U_{13} 0·0006 (1)
			$U_{12}=U_{23}=0{\cdot}0$

diffraction study for tetragonal V_2H recently gave information on the H-atom distribution not only in octahedral interstices but also in the neighbouring tetrahedral ones of the fundamental body-centered V lattice (Kajitani & Hirabayashi, 1985*a*).

The refinement functions in the case of monoclinic V_2H remain rather large compared with those in the case of tetragonal V_2H. This is probably due to the presence of microtwins less than 1 μm in width, which were caused by accumulated stress on the transformation from the α to the β_1 phase because of the large tetragonality (c_0/a_0) and the lattice distortion of the monoclinic structure (Takano & Suzuki, 1974).

The present study has indicated that two different crystal structures and correspondingly two different arrangements of H atoms are possible for β_1-V_2H, depending on the conditions for growth of the crystal. For the sake of comparison, the crystal data for the host V lattice are given in Table 4. The axial angle α_0 of monoclinic V_2H significantly differs from 90°. This result may arise from the fact that H atoms lie only on the $(0\bar{1}1)$ plane among the equivalent $\{101\}$ planes of the fundamental lattice. In spite of the different ordered arrangements of H atoms, the crystal data other than α_0 are not very different for the two structures. This may be because atomic interaction energies are not very different for the two structures unless four-body correlations are taken into consideration (Kajitani & Hirabayashi, 1985*b*). However, it is not clear why the crystal growth under tensile stress prefers the arrangement of H atoms in Fig. 1(a) while that grown under no stress prefers the other, Fig. 1(b).

Table 4. *Crystal data of fundamental body-centered lattice in tetragonal and monoclinic* β_1-V_2H

Figures in parentheses are standard deviations from the least-squares calculation and do not represent absolute accuracy.

	Tetragonal	Monoclinic	Tetragonal ¶
Tensile stress on crystal growth (MPa)	$1{\cdot}1\times10^1$	0·0	$2{\cdot}9\times10^2$
a_0 (Å)	3·0006 (2)	3·0011 (2)	3·0174 (2)
c_0 (Å)	3·3094 (4)	3·3086 (3)	3·4358 (4)
α_0 (°)	90	90·251 (8)	90
c_0/a_0	1·1029 (2)	1·1025 (2)	1·1387 (2)
Static displacement of V atom (Å)	0·1133 (2)	0·1094 (5)*	0·0225 (18)
Shortest atomic distance (Å)			
V—V	2·5550 (4)	2·5662 (8)†	2·730 (1)
V—H	1·7680 (3)	1·7638 (6)†	1·699 (2)
Maximum and minimum thermal vibrational r.m.s. displacement (Å)			
V atom $u_{\max}$	0·0813 (7)	0·095 (2)‡	0·104 (1)
$u_{\min}$	0·0739 (6)	0·079 (2)‡	0·064 (2)
$B_{\rm eq}$ of V atom (Å^2)§	0·460 (7)	0·48 (2)	0·65 (3)

* Displacement of V atom averaged between those of V(1) and V(2).

† Atomic distances averaged between those for V(1) and V(2).

‡ R.m.s. displacement calculated from V(1) atom.

§ Equivalent isotropic thermal parameter $B_{\rm eq}=(8\pi^2/3)\sum_{ij}U_{ij}$.

¶ Crystal data obtained in previous work (Noda, Kajitani, Hirabayashi & Sato, 1985).

It is widely recognized that the cell dimension of the fundamental lattice depends on a deviation in composition from stoichiometric V_2H (Asano & Hirabayashi, 1979). Table 4 includes tensile stress value and crystal data for tetragonal V_2H obtained in previous work (Noda, Kajitani, Hirabayashi & Sato, 1985). It must be emphasized here that the crystal data also depend on the tensile stress and that the difference between the present and previous work exists along the [001] direction of the tensile axis. The smallness of the displacement ($0{\cdot}02_3$ Å) of the V atom is consistent with the larger tetragonality induced by larger tensile stress, since the H atom might easily occupy the elongated large octahedral interstices in the [001] direction. Thus, tetragonal V_2H can be attributed to the stress-induced phase.

It is to be noted that the crystal structure of the deuteride β-V_2D is monoclinic whether growth is under tensile stress or not (Okada, Asano & Hirabayashi, 1980; Noda, Kajitani, Hirabayashi & Sato, 1985).

The authors express their thanks to Professor M. Hirabayashi and Dr T. Kajitani for discussions. The X-ray work was performed under the Visiting Researchers Program of the Institute for Solid State Physics, University of Tokyo, provided for one of the authors (YN). The calculations were carried out using a NEAC ACOS1000 computer at the Computer Center of Tohoku University.

References

ASANO, H., ABE, Y. & HIRABAYASHI, M. (1976). *J. Phys. Soc. Jpn*, **41**, 974-976.

ASANO, H. & HIRABAYASHI, M. (1979). *Z. Phys. Chem.* (*Frankfurt am Main*), **114**, 1-19.

COPPENS, P., GURU ROW, T. N., LEUNG, P., STEVENS, E. D., BECKER, P. J. & YANG, Y. W. (1979). *Acta Cryst.* A**35**, 63-72.

COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A**26**, 71-83.

International Tables for X-ray Crystallography (1959). Vol. II. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

International Tables for X-ray Crystallography (1969). Vol. I, 3rd ed. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1974). Vol IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

KAJITANI, T. & HIRABAYASHI, M. (1985*a*). *Z. Phys. Chem.* (*Frankfurt am Main*), **145**, 281-296.

KAJITANI, T. & HIRABAYASHI, M. (1985*b*). Private communication.

KOIKE, S. & SUZUKI, T. (1981). *Acta Metall.* **29**, 553-565.

MOSS, S. C. (1983). *Electronic Structure and Properties of Hydrogen in Metals*, edited by P. JENA & C. B. SATTERTHWAITE, pp. 153-163. New York: Plenum.

NODA, Y., KAJITANI, T., HIRABAYASHI, M. & SATO, S. (1985). *Acta Cryst.* C**41**, 1566-1571.

OKADA, I., ASANO, H. & HIRABAYASHI, M. (1980). *Trans. Jpn Inst. Met. Suppl.* **21**, 89-92. *Hydrogen in Metals. Proc. Minakami, Japan.*

TAKANO, S. & SUZUKI, T. (1974). *Acta Metall.* **22**, 265-274.

WANAGEL, J., SASS, S. L. & BATTERMAN, B. W. (1972). *Phys. Status Solidi A*, **10**, 49-57.

Acta Cryst. (1986). B**42**, 533-538

Normal Coordinate Analysis of Metal–Metal Quadruple Bonds Using a More Complete Force Field

BY E. M. LARSON, T. M. BROWN AND R. B. VON DREELE*

Department of Chemistry, Bateman Science Center, Arizona State University, Tempe, Arizona 85287, *USA*

(*Received* 10 *May* 1985; *accepted* 17 *April* 1986)

Abstract

Normal coordinate analyses have been performed for $Mo_2(O_2CCH_3)_4$, $Mo_2Cl_8^{4-}$, $Re_2(O_2CCH_3)_4Cl_2$ and $Re_2Cl_8^{2-}$ by treating each compound as an isolated molecule with $4/mmm$ (D_{4h}) symmetry and also using the positions found in their respective crystal structures. In all cases the molecules were modelled as flexible structures with the acetate methyl groups taken as point masses. Calculated and experimental frequencies are reported along with valence bond and angle force constants. The normal modes for the $4/mmm$ models are shown and discussed for the bands observed in the experimental IR and Raman spectra of the Mo compounds. As a consequence of considering the bridging ring systems and partial Coulombic charges in the calculations for the isolated molecules and ions, values of 2·0, 2·0, 1·1 and 1·9 N m^{-1}, respectively, are obtained for the $M\equiv M$ force constants. When the intermolecular interactions in the solids are considered, somewhat lower values, 1·8, 1·7, 1·0 and 1·9 N m^{-1}, respectively, are obtained.

Introduction

Normal coordinate analyses have been performed for polycyclic inorganic compounds but little has been done with systems having both multiple metal-metal bonds and bridging ring systems. An early analysis was performed on $Cr_2(O_2CCH_3)_4.2H_2O$ by Costa, Pauluzzi & Puxeddu (1957) to determine the force constants in the acetate groups but only the C—C and C—O stretching force constants were considered; the metal-metal bond and metal-ligand interactions were ignored. Vibrational analyses for compounds with bridging acetates have recently been published, but no normal coordinate calculations were carried out and the compounds did not have metal-metal bonds (Johnson, Cannon & Powell, 1981, 1982). The vibrational spectrum of $Cu_2(O_2CCH_3)_4.2H_2O$ has been examined, but again no normal coordinate analysis was done and the Cu-Cu interaction is considered to be nonbonding (Shriver, Mathey & Greig, 1982). The compounds to be examined here were previously subjected to normal coordinate analysis (Bratton, Cotton, Debeau & Walton, 1971; Ketteringham, Oldham & Peacock, 1976), but only the M_2X_8 portion of the molecules was used and the effects of the bridging rings and residual charges were ignored. We have chosen to do a more complete vibrational analysis of these compounds to explore the effects of the acetate bridges and residual charges on their molecular vibrations with a view toward obtaining a more accurate picture of the multiple metal-metal bond. Although we were able to obtain all the spectra needed for this study from the literature, there were conflicting Raman spectra for

---

* To whom all correspondence should be addressed. Present address: Los Alamos National Laboratory, CHM1 MS G740, Los Alamos, New Mexico 97544, USA.

0108-7681/86/060533-06$01.50 © 1986 International Union of Crystallography