

the bands to **1** or **4** stand the test of time, it immediately follows that the appearance of four absorptions below  $1700\text{ cm}^{-1}$  excludes the possibility of the square ring since group theory predicts for this geometry (point group  $D_{4h}$ ) only three IR-active vibrations in addition to the C—H stretching vibration which appears at  $\sim 3000\text{ cm}^{-1}$ . The band at  $1523\text{ cm}^{-1}$  which shifts to  $1456\text{ cm}^{-1}$  upon deuteration is undoubtedly due to the C=C stretching vibration and corroborates this conclusion.

The spectra presented are consistent with a rectangular geometry for **1** and **4**, point group  $D_{2h}$ . The application of the product rule<sup>13</sup> to the present data leads to the following symmetry assignment of vibrations A-D and A'-D' (see Table I): the pairs of vibrations B and C and B' and C' have  $B_{2u}$  symmetry<sup>14</sup> (product rule ratio: theoretical 1.927, observed 1.918 where the C—H and C—D stretching frequencies are assumed to have the harmonic ratio 1.363); D and D' are the sole  $B_{3u}$  out-of-plane hydrogen and deuterium vibrations (product rule ratio: theoretical 1.363, observed 1.357); and finally the C=C stretching vibrations (A and A') and unobserved vibrations (vide infra) that correspond primarily to H—C—C and D—C—C bending motions have  $B_{1u}$  symmetry. The isotope shifts indicate that B ( $1240\text{ cm}^{-1}$ ) is due largely to H—C—C in-plane bending motion and clearly not primarily to the C—C stretching motion which contributes mainly to C ( $723\text{ cm}^{-1}$ ). In **4** the vibrations B' and C' ( $1043$  and  $609\text{ cm}^{-1}$ ) are both heavy mixtures of these two motions.<sup>15,16</sup> Thus the conclusion derived from the earlier IR analysis completely loses its ground.<sup>17</sup> It is already noted that one  $B_{1u}$  vibration has not been identified. Although the presence of some very weak absorptions at  $\sim 1000\text{ cm}^{-1}$  in the case of **1** and at  $\sim 750\text{ cm}^{-1}$  in **4** is indicated in the spectra, we judge that their intensities are too small to be confirmed with the present sophistication of instrumentation.

Obviously, the number of observed bands enables one to exclude the geometries of symmetry higher than that allowed by group theory, but does not necessarily define the exact symmetry of the molecule. The present study, at minimum, provides the answer to the recent controversial cyclobutadiene problem and the chemistry of this system has now become mutually consistent. The evidence, both theoretical and experimental, points to the conclusion that the cyclobutadiene ring in the ground state is not square but very likely rectangular.<sup>18,19</sup>

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- The geometry suggested earlier<sup>2a</sup> and a set of reasonable force constants reproduced the observed frequencies well through a GF normal coordinate calculation.  $^{13}\text{C}_4\text{H}_4$ :  $B_{1u}$ , 1540, 974 (not observed);  $B_{2u}$ , 1223, 740;  $B_{3u}$ , 574.  $\text{C}_4\text{D}_4$ :  $B_{1u}$ , 1455, 713 (not observed);  $B_{2u}$ , 1054, 604;  $B_{3u}$ , 422. Assignments are as reported in the text. Internal coordinates: 4 C—H, 2 C=C, 2 C—C, 4 H—C—C, 4 H—C=C, 4 out-of-plane H—C—C<sub>2</sub>. Geometry assumed:  $r_{\text{C—C}} = 1.37\text{ \AA}$ ,  $r_{\text{C—C}} = 1.51\text{ \AA}$ ,  $r_{\text{C—H}} = 1.08\text{ \AA}$ , H—C—C angle =  $135^\circ$ . Force constants: C—H, 4.85; C=C, 7.425; C—C, 2.55 (all mdyn  $\text{\AA}^{-1}$ ); H—C—C and H—C=C, 0.367 mdyn  $\text{\AA}$ ; out-of-plane H—C—C<sub>2</sub>, 0.2105 mdyn  $\text{\AA}$  (all interaction force constants 0.0).
- The isotope shifts are definitely inconsistent with the assignment of B ( $1240\text{ cm}^{-1}$ ) primarily to C—C stretching vibration.
- This  $1241\text{ cm}^{-1}$  band shifts to  $1237\text{ cm}^{-1}$  in the spectrum of  $^{13}\text{CC}_3\text{H}_4$ ,<sup>5c</sup> but this result alone contributes very little to the assignment.
- All the deuterated photoprecursors were at minimum 98% rich in deuterium content and full experimental details of the syntheses of these compounds and the matrix work are available on request. (F.A.S.-B., Ph.D. Thesis, University of Alberta.)
- The authors thank Drs. K. Sakan, R. L. Sobczak, and S. Ohta for their preparations of deuterated precursors, Mr. A. Clement for his technical assistance, Professor G. L. Closs for valuable suggestions, and the National Research Council of Canada for financial support.
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## Isomerism and Charge Distribution in Mixed-Metal Polyoxoanion Clusters: Oxygen-17 Nuclear Magnetic Resonance Structure Determinations of *cis*- $\text{V}_2\text{W}_4\text{O}_{19}^{4-}$ and *cis*- $\text{HV}_2\text{W}_4\text{O}_{19}^{3-}$

Sir:

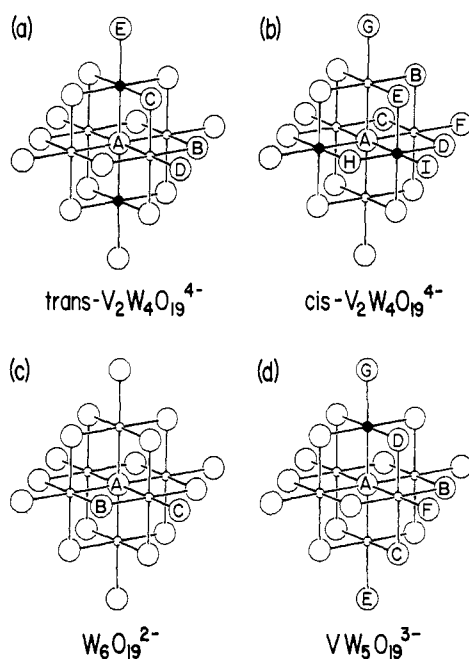
Mixed-metal polyoxoanion clusters have recently attracted attention as reversible oxidants in the homogeneous catalytic oxidation of olefinic and aromatic hydrocarbons.<sup>1-3</sup> Characterization of structure and charge distribution clearly provides a first step toward understanding the reactivity of these species. Although x-ray crystallographic studies have characterized the overall metal-oxygen frameworks in several mixed-metal polyanions,<sup>4-6</sup> in no case have the relative positions of the different metal atoms within the framework been determined. Infrared,<sup>7</sup>  $^{51}\text{V}$  NMR,<sup>8-10</sup>  $^{31}\text{P}$  NMR,<sup>9-11</sup> and  $^{17}\text{O}$  NMR<sup>6,12,13</sup> studies have likewise failed to unambiguously establish metal atom configurations for specific mixed-metal isomers. We report here an  $^{17}\text{O}$  NMR study of  $\text{V}_2\text{W}_4\text{O}_{19}^{4-}$  which establishes a *cis* relationship between vanadium atoms in its octahedral metal array, and demonstrates that negative charge on the surface of the cluster is concentrated on the unique oxygen atom bonded to both vanadiums.

X-ray crystallography has provided a structural model for  $\text{V}_2\text{W}_4\text{O}_{19}^{4-}$  in  $\alpha\text{-(CN}_3\text{H}_6)_4\text{V}_2\text{W}_4\text{O}_{19}$  consistent with the *cis* or *trans* structures shown in Figure 1a and 1b, or a mixture of the two.<sup>4</sup> Assuming that the pertinent resonances may be observed, sufficiently resolved, and assigned,  $^{17}\text{O}$  NMR spectroscopy should allow assignment of a *cis* or *trans* structure on the basis of one or more of the following structural features: (1) only the *cis* structure possesses an  $\text{OV}_2$  oxygen, i.e., an oxygen bonded to two vanadiums, (2) all OW oxygens bonded to a single tungsten are symmetry equivalent in the *trans* structure as are the  $\text{OW}_2$  oxygens bonded to two tungstens, whereas the *cis* structure contains two nonequivalent types of

**Table I.**  $^{17}\text{O}$  NMR Spectral Data

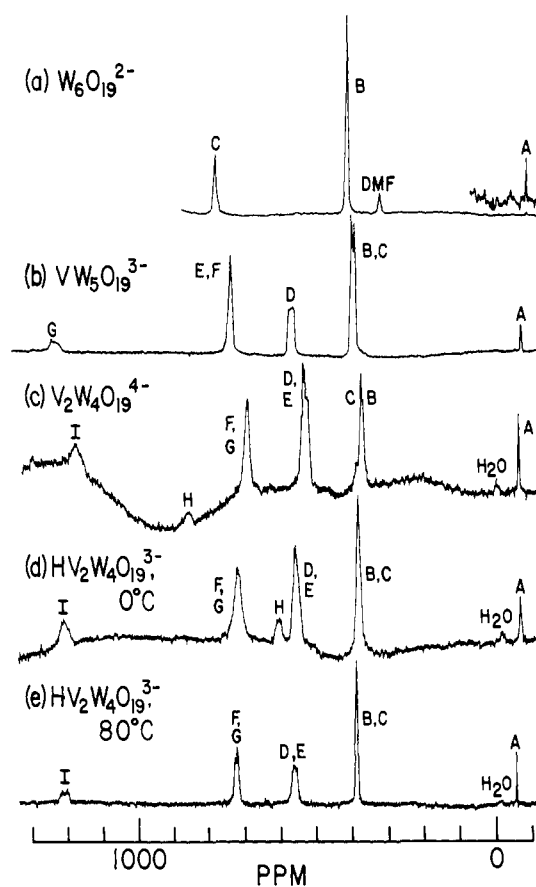
Anion <sup>a</sup>	Chemical shifts, <sup>b</sup> assignments, <sup>c</sup> line widths <sup>d</sup>						
	OV	OV <sub>2</sub>	OW	OV <sub>2</sub> H	OVW	OW <sub>2</sub>	OM <sub>6</sub>
(a) $\text{W}_6\text{O}_{19}^{2-}$ <sup>e</sup>			772 (C) [99]			413 (B) [66]	-81 (A) [32]
(b) $\text{VW}_5\text{O}_{19}^{3-}$ <sup>f</sup>	1217 (G) [454]		731 (E, F) [115]		562 (D) [266]	395, 389 (B, C) [79], [79]	-75 (A) [28]
(c) $\text{V}_2\text{W}_4\text{O}_{19}^{4-}$ <sup>g</sup>	1162 (I) [423]	848 (H) [351]	687 (F, G) [207]		530 (D, E) [286]	384 (C), 371 (B) [h], [134]	-65 (A) [41]
(d) $\text{HV}_2\text{W}_4\text{O}_{19}^{3-}$ <sup>i</sup>	1208 (I) [353]		723 (F, G) [302]	610 (H) [281]	564 (D, E) [209]	391 (B, C) [136]	-60 (A) [64]
(e) $\text{HV}_2\text{W}_4\text{O}_{19}^{3-}$ <sup>j</sup>	1203 (I) [411]		729, 722 (F, G) [164] <sup>k</sup>		567 (D, E) [245]	393 (B, C) [43]	-53 (A) [14]

<sup>a</sup> Letters preceding anions corresponds to labels on spectra in Figure 2. <sup>b</sup> Positive chemical shift in parts per million downfield from pure  $\text{H}_2\text{O}$  at 25 °C,  $\pm 3$  ppm for all except OV resonances,  $\pm 6$  ppm for OV resonances. <sup>c</sup> In parenthesis; see Figure 1 for labeling scheme. <sup>d</sup> In brackets under chemical shift value,  $\pm 15$  Hz. <sup>e</sup>  $(n\text{-Bu}_4\text{N})_2\text{W}_6\text{O}_{19}$ , 2%  $^{17}\text{O}$ , 0.087 M in DMF at 30 °C. <sup>f</sup>  $(n\text{-Bu}_4\text{N})_3\text{VW}_5\text{O}_{19}$ , 18%  $^{17}\text{O}$ , 0.064 M in  $\text{CH}_3\text{CN}$  at 30 °C. <sup>g</sup>  $(n\text{-Bu}_4\text{N})_4\text{V}_2\text{W}_4\text{O}_{19}\cdot 2\text{H}_2\text{O}$ , 4%  $^{17}\text{O}$ , 0.089 M in  $\text{CH}_3\text{CN}$  at 30 °C. <sup>h</sup> Shoulder. <sup>i</sup>  $(n\text{-Bu}_4\text{N})_3\text{HV}_2\text{W}_4\text{O}_{19}\cdot \text{H}_2\text{O}$ , 5%  $^{17}\text{O}$ , 0.15 M in  $\text{CH}_3\text{CN}$  at 0 °C. <sup>j</sup> Same sample as in *i*, at 80 °C. <sup>k</sup> Combined line width of F and G resonances.



**Figure 1.** Idealized structures of (a)  $\text{trans-V}_2\text{W}_4\text{O}_{19}^{4-}$  ( $D_{4h}$ ), (b)  $\text{cis-V}_2\text{W}_4\text{O}_{19}^{4-}$  ( $C_{2v}$ ), (c)  $\text{W}_6\text{O}_{19}^{2-}$  ( $O_h$ ), and (d)  $\text{VW}_5\text{O}_{19}^{3-}$  ( $C_{4v}$ ). Large open circles represent oxygen atoms, small open circles represent tungsten atoms, and small filled circles represent vanadium atoms. Within each structure, one member of each symmetry equivalent set of oxygen atoms is labeled.

OW oxygens and two nonequivalent types of  $\text{OW}_2$  oxygens, and (3) all OVW oxygens are equivalent in the *trans* structure, but two nonequivalent types are found in the *cis* structure. Resonances for the  $\text{V}_2\text{W}_4\text{O}_{19}^{4-}$  ion can of course be assigned only after delineation of the chemical shift ranges for oxygens in similar OV, OW,  $\text{OV}_2$ ,  $\text{OW}_2$ , and OVW environments. This was accomplished by measuring spectra for the  $\text{W}_6\text{O}_{19}^{2-}$  and  $\text{VW}_5\text{O}_{19}^{3-}$  anions<sup>14,15</sup> (see Figure 2a and 2b). Resonances for  $\text{W}_6\text{O}_{19}^{2-}$  were assigned by analogy with procedures used for assigning resonances in the isostructural<sup>16</sup>  $\text{Mo}_6\text{O}_{19}^{2-}$  anion.<sup>17</sup> For the  $\text{VW}_5\text{O}_{19}^{3-}$  anion,<sup>18</sup> resonances of oxygens bonded to vanadium are readily identified by their unusual line shapes caused by  $^{51}\text{V}$ - $^{17}\text{O}$  spin-spin coupling to  $S = 7/2$   $^{51}\text{V}$  nuclei.<sup>19</sup> Assignment of terminal and bridging oxygen resonances for  $\text{VW}_5\text{O}_{19}^{3-}$  follows from consideration of analogous assignments for the  $\text{W}_6\text{O}_{19}^{2-}$  anion and the  $\text{V}_{10}\text{O}_{28}^{6-}$  anion.<sup>20</sup> With these data in hand, the spectrum of the  $\text{V}_2\text{W}_4\text{O}_{19}^{4-}$  anion<sup>21</sup> may be assigned as shown in Figure 2c. The spectrum clearly



**Figure 2.** 13.5-MHz  $^{17}\text{O}$  NMR spectra of hexamallate anions discussed in the text. See Table I for spectral data. Resonances are assigned using the lettering schemes given in Figure 1b-d.

corresponds to the *cis* isomer since (1) the 848-ppm resonance is in the range expected for  $\text{OV}_2$  oxygens<sup>20</sup> and (2) two resonances are observed in the  $\text{OW}_2$  region. Although data presented thus far do not rule out the presence of smaller amounts of *trans* isomer, we view this possibility as highly unlikely in light of the qualitative agreement of relative intensities with those anticipated for the *cis* isomer. Data obtained for the protonated anion (see below) support this contention.

As demonstrated elsewhere for the  $\text{V}_{10}\text{O}_{28}^{6-}$  anion,<sup>20</sup>  $^{17}\text{O}$  NMR is a sensitive probe for the determination of protonation sites and hence surface charge distribution on polyoxoanion clusters. When an oxygen atom is protonated, its metal-oxygen bonds are weakened, causing its  $^{17}\text{O}$  NMR resonance to shift

upfield. Comparison of the  $V_2W_4O_{19}^{4-}$  spectrum discussed above with the spectrum of the  $HV_2W_4O_{19}^{3-}$  anion<sup>22</sup> measured at 0 °C (see Figure 1d) reveals an upfield shift of only the  $OV_2$  resonance upon protonation. This pronounced change in chemical shift unambiguously identifies the  $OV_2$  oxygen in the  $V_2W_4O_{19}^{4-}$  cluster as the protonation site. Note that all resonances except the  $OV_2$  resonance in  $V_2W_4O_{19}^{4-}$  shift downfield upon protonation of the cluster. This downfield shift reflects a strengthening of metal-oxygen bonds and a concomitant reduction of negative charge on the oxygens in question.

When spectra of  $HV_2W_4O_{19}^{3-}$  are observed at elevated temperatures (see Figure 2e), two significant consequences of the reduced rate of  $^{17}O$  and  $^{51}V$  quadrupole relaxation are observed. First, the line widths of resonances for the OW oxygens are sufficiently narrowed as to allow resolution of the resonances for the two nonequivalent OW oxygen types. Their approximately equal intensities add support to the contention that the sample contains only the *cis*- $V_2$  isomer. Second, the OV, OVW, and  $OV_2H$  resonances are broadened owing to  $^{51}V$ - $^{17}O$  spin-spin coupling.<sup>23</sup> It is possible that reported failures<sup>6,12,13</sup> to observe resonances for OV, OVMO, and OVW resonances in other mixed-metal polyoxoanions were due to this line-broadening effect. We are currently attempting to measure vanadium-decoupled  $^{17}O$  NMR spectra in an effort to obtain more highly resolved spectra.

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- $[(n-C_4H_9)_4N]_2W_6O_{19}$  was obtained by refluxing  $[(n-C_4H_9)_4N]_4W_{10}O_{32}$  in  $CH_3OH/CH_3CN$ . Anal. ( $C_{32}H_{72}N_2O_{19}W$ ) C, H, N, W.
- $[(n-C_4H_9)_4N]_3VW_5O_{19}$  was obtained by refluxing  $[(n-C_4H_9)_4N]_4W_{10}O_{32}$  and  $[(n-C_4H_9)_4N]_4V_2O_7$  (1:1 mol ratio) in  $CH_3OH/CH_3CN$ , precipitating the product with ether, and recrystallizing in  $CH_3CN$ . Anal. ( $C_{48}H_{108}N_3O_{19}VW_5$ ) C, H, N, V, W.
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- $[(n-C_4H_9)_4N]_3HV_2W_4O_{19} \cdot H_2O$  was obtained by acidifying an aqueous solution of  $Na_2WO_4$  and  $NaVO_3$  (2:1 mol ratio) to pH 5 with HCl, obtaining a

crude precipitate by addition of  $(n-C_4H_9)_4NBr$ , and recrystallizing the precipitate from  $CH_3CN$ . Anal. ( $C_{48}H_{110}N_3O_{20}V_2W_4$ ) C, H, N, V, W.

- The resonances for oxygens bonded to one vanadium are presumably broadened much less than the resonance for the oxygen bonded to two vanadiums since, in the limit of slow  $^{51}V$  quadrupole relaxation at high temperature, the former should yield eight resolved components whereas the latter should yield fifteen components due to coupling to the two  $S = 7/2$   $^{51}V$  nuclei. Although line-shape simulations have not been calculated for a nucleus coupled to two  $S = 7/2$  quadrupolar nuclei as a function of quadrupole relaxation rate, results obtained for related systems<sup>24</sup> support this interpretation. Broadening of the  $OV_2H$  resonance cannot be due to rapid oxygen exchange with water since the water resonance is observed at 80 °C.
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- Fellow of the Alfred P. Sloan Foundation, 1976-1978.

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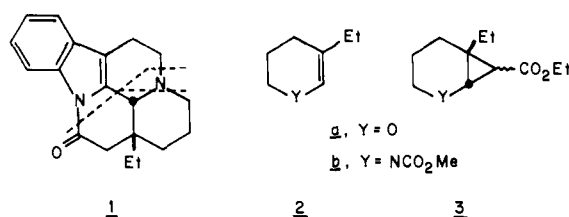
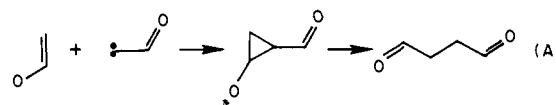
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## Short Syntheses of Eburnamonine via $\beta$ -Oxycyclopropylcarbonyl and Related Intermediates

Sir:

The two-step construction of  $\gamma$  diketones outlined in sequence A has formed the basis of recent syntheses of cyclopentanoid terpenic and other natural products.<sup>1</sup> It seemed plausible that the scheme could be adapted to  $\gamma$ -imino ketone preparation by way of the introduction of nitrogen at some stage of the reaction sequence<sup>2</sup> and hence its applicability extended to the formation of alkaloids. The two syntheses of eburnamonine (**1**)<sup>3</sup> shown involve this concept in the production of the nonindole portion of the alkaloid (cf. dotted lines in **1**).



Dilute acid hydrolysis of esters **3a**, prepared previously by the copper-assisted decomposition of ethyl diazoacetate in dihydropyran **2a**,<sup>4</sup> yielded (93%) lactone **4**<sup>5</sup> (bp 82-84 °C (0.2 Torr); IR (neat) 5.58  $\mu$ ;  $^1H$  NMR  $\delta$  ( $CDCl_3$ ) 0.92 (t, 3,  $J = 7$  Hz), 1.3-1.8 (m, 6), 2.36 (s, 2), 3.5-4.0 (m, 2), 5.28 (s, 1)) whose treatment with boron tribromide in methylene chloride (room temperature, 14 h) gave (71%) dibromides **5** and **6** (mixture bp 121-124 °C (0.007 Torr); IR (neat) 5.52  $\mu$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.93, 0.96 (t each, total 3,  $J = 7$  Hz), 1.4-2.1 (m, 6), 2.41, 2.46 (s each, total 2), 3.2-3.6 (m, 2), 6.30, 6.31 (s each, total 1)). Hydrolysis (1% hydrochloric acid, dioxane, 80 °C, 20 h) of the mixture produced a bromo- $\gamma$ -lactol, whose interaction with tryptamine hydrochloride in anhydrous dimethyl sulfoxide (stirring 12 h with 3- $\text{\AA}$  sieves, 55 °C) led (78%) to carbinolamine lactone **7**:<sup>6</sup> IR ( $CHCl_3$ ) 2.87, 5.76  $\mu$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.78 (t, 3), 1.2-1.8 (m, 6), 2.1-2.5 (m, 2), 2.6-3.1 (m, 6), 5.07 (s, 1), 6.9-7.6 (m, 5), 8.39 (s, 1).

Reduction of 3-acetyl-1,4,5,6-tetrahydropyridine (**8a**)<sup>7</sup> with lithium aluminum hydride (refluxing dioxane, 8 h)<sup>8</sup> afforded (15%) 3-ethyl-2-piperidine (**8b**), whose immediate acylation