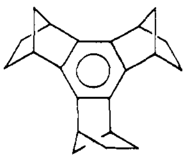
showed four sets of peaks in its ^{13}C NMR spectrum at 136.2 and 123.72 (s), 48.69 and 48.44 (t), 41.21 and 41.11 (d), and 27.43 and 27.12 (t) ppm, indicating that it was the syn–anti–syn isomer, **7**.[10] The ^{13}C NMR spectra of the minor isomer, mp 175–180 °C, showed only four absorptions at 136.19 (s), 48.91 (t), 41.05 (d), and 27.09 (t) ppm, indicating that it was the all-syn isomer, **8**.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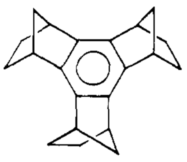
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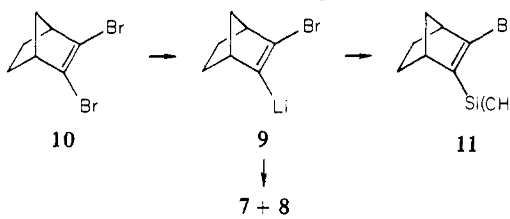
The formation of trimers, in yields ranging from 2–44%, has been used as evidence for the formation of cyclooctyne,[11] cycloheptyne,[9,12] cyclohexyne,[9] and cyclopentyne.[5] We suggest that the isolation of **7** and **8** provides equally strong evidence for the transitory existence of bicyclo[2.2.1]hept-2-yne (**3**). We believe that this is the most strained acetylene derivative prepared thus far.

The results above raised the question of why **2** appeared to decompose at 25 °C under the conditions of excess *n*-butyllithium[1] but was stable at 25 °C when prepared as described above. We felt that the decomposition of **2** might be promoted by excess organolithium reagents. This was substantiated by the observation that addition of *tert*-butyllithium, methyllithium, or *n*-butyllithium to **2** promoted its dehydrohalogenation at 25 °C. Both *tert*-butyllithium and methyllithium promoted the conversion of **2** into high molecular weight oligomers and a mixture of **7** and **8**. In contrast, *n*-butyllithium promoted the conversion of **2** to 2-*n*-butylbicyclo[2.2.1]hept-2-ene which was the major product identified previously.[1]

Lastly, we examined the stability of **9**. Unfortunately, **9** could not be prepared through an acid–base reaction of 2-bromobicyclo[2.2.1]hept-2-ene with an organolithium reagent due to the propensity of the bromide to undergo halogen–metal exchange reactions. Thus, **10** was used as the precursor.[13] Treatment of **10** with *n*-butyllithium in tetrahydrofuran-hexane at −78 °C gave **9**. When a solution of **9** was warmed quickly to 25 °C, only intractable material was formed. In contrast, addition of (chlorotrimethyl)silane to a solution of **9** at −78 °C, gave a 90% yield of **11**, which substantiated the intermediacy of **9**.[14] Since acetylene trimerization is known to be catalyzed by certain transition-metal complexes,[15] we questioned whether the addition of such complexes to a solution of **9** at −78 °C followed by warming would produce **7** and **8**. When a solution of **9** was treated with nickelocene[16] and allowed to warm to room temperature, a 37% yield of a mixture of **7** and **8** was obtained. Other transition-metal derivatives which promoted formation of the trimer of bicyclo[2.2.1]hept-2-yne were nickel(II) chloride, iron(III) chloride, copper(I) iodide, copper(II) chloride, and cyclopentadienylbis(triphenylphosphine)cobalt.[15]



10 9 11

7 + 8

Acknowledgment. We are indebted to the National Science Foundation for Grant CHE78-10231 which supported this investigation.

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[10] Theoretically, one would expect three separate resonances for the bridgehead carbons, three different aromatic carbons, three different ethanobridge carbons, and two different methanobridge carbons. However, in view of the small chemical shift differences within the sets, some degeneracy might be expected.

[11] G. Wittig and S. Fischer, *Chem. Ber.*, **105**, 3542 (1972).

[12] G. Wittig and J. Meske-Schüller, *Justus Liebigs Ann. Chem.*, **711**, 65 (1968).

[13] The synthesis of **10** will be reported elsewhere: P. G. Gassman and I. A. Gennick, *J. Org. Chem.*, in press.

[14] In a similar manner, treatment of **9** with iodine gave a 60% yield of 2-bromo-3-iodobicyclo[2.2.1]hept-2-ene.

[15] K. P. C. Vollhardt, *Acc. Chem. Res.*, **10**, 1 (1977).

[16] W. L. Jolly and D. J. Chozan, *Inorg. Synth.*, **11**, 122 (1968).

[17] National Science Foundation Predoctoral Fellow, 1975–1978; Louise T. Dosdall Graduate Fellow, 1978–1979; Lubrizol Foundation Fellow, Summer 1979.

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Mixed Valence and Magnetically Coupled Vanadate Domains in Heteropoly Tungstate Anions

Sir:

The analogy between heteropoly anions and metal oxide lattices vis-à-vis structures and catalytic properties has been recognized for several years.[1] Partially reduced polyanions ("heteropoly blues")[2] are of considerable interest because, in principle, they provide insight into electron mobility (semiconduction) and magnetic exchange interactions in metal-oxide-like environments. Analysis of such processes in heteropoly blues and oxides has been complicated by the existence of numerous "intramolecular" pathways for electron transfer and magnetic coupling. We have recently developed stereospecific syntheses of certain mixed-metal polyanions and can use these to explore electronic interactions between a small number of adjacent metal atoms in a polyanion. We report here the first ESR and magnetic data for complexes of this sort in which unpaired electrons are restricted to two or three oxygen-bridged vanadium atoms.

The complexes are α-1,2-SiV$_2$W$_{10}$O$_{40}{}^{6-}$ (**1**) and α-1,2,3-SiV$_3$W$_9$O$_{40}$H^{6-} (**2**) and their reduced forms. It is believed that the vanadium atoms in **1** and **2** occupy adjacent corner-sharing "octahedral" sites in the Keggin structure (Figure 1).[3] Controlled potential reduction of **1** and **2** yields green α-SiV^{IV}V^{V}W$_{10}$O$_{40}{}^{7-}$ (**1a**) and α-SiV^{IV}V$_2{}^{V}$W$_9$O$_{40}$H$_x{}^{8-x}$ (**2a**) with the ESR spectra shown in Figure 2. The 15-line spectrum (g = 1.966, a = 51 G) for **1a** is consistent with an electron interacting with two equivalent vanadium-51 nuclei ($I = {}^7/_2$)[4] and stands in contrast to the spectrum of a mixture of isomers of α-PV^{IV}V^{V}W$_{10}$O$_{40}{}^{6-}$ which consists of both 8- and 15-line components.[5] The ESR spectrum of **2a** consists of more than 40 equally spaced hyperfine lines (g = 1.960) and has been interpreted according to the stick diagram shown in Figure 2. The interpretation assumes a spectrum of eight equally intense lines (a_1 = 68 G) each one of which is split into

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[1] Baker, L. C. W. In "Advances in the Chemistry of Coordination Compounds"; Kirschner, S., Ed.; Macmillan: New York, 1961; p 604.

[2] Pope, M. T. In "Mixed Valence Compounds in Chemistry, Physics and Biology"; Brown, D. B., Ed.; Reidel: Amsterdam, 1980.

[3] The complexes are prepared as potassium salts from α-SiW$_9$O$_{34}$H^{8-} and VO$_3{}^-$ (**2**) or partially hydrolyzed α-SiW$_{12}$O$_{40}{}^{4-}$ and VO^{2+} (**1b** and subsequent oxidation to **1**). Details will be given in forthcoming publications. Analyses: K, Si, V, W, H$_2$O. ^{51}V FT NMR spectra (24 and 71 MHz) consist of a single symmetrical line for each complex. At 80 °C, pH 2, chemical shifts from VOCl$_3$ and line widths are **1**, −536 ppm, 66 Hz; **2**, −566 ppm, 130 Hz. On the basis of the structure of the precursor ion, the vanadium atoms in **1** and **2** occupy the sites shown in Figure 1. Alternative structures in which the vanadium atoms occupy adjacent edge-shared octahedra would also be consistent with the data of the present paper, but are considered unlikely.

[4] To our knowledge, the only other example of a 15-line mixed-valence vanadium ESR spectrum was recently reported for μ-oxybis(nitrilotriacetato)oxovanadate(IV,V): Nishizawa, M.; Hirotsu, K.; Ooi, S.; Saito, K. *J. Chem. Soc., Chem. Commun.* **1979**, 707. We are unable to say with present data whether the electron is delocalized or rapidly hopping in these cases.

[5] Pope, M. T.; O'Donnell, S. E.; Prados, R. A. *J. Chem. Soc., Chem. Commun.*, **1976**, 85.

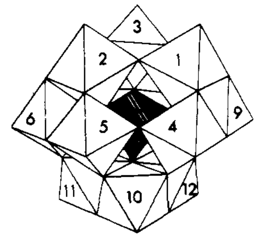

Figure 1. Polyhedral representation of the Keggin structure with proposed IUPAC numbering scheme for metal atoms. Complexes **1** and **2** contain vanadiums in sites 1 and 2 and 1, 2, and 3, respectively.

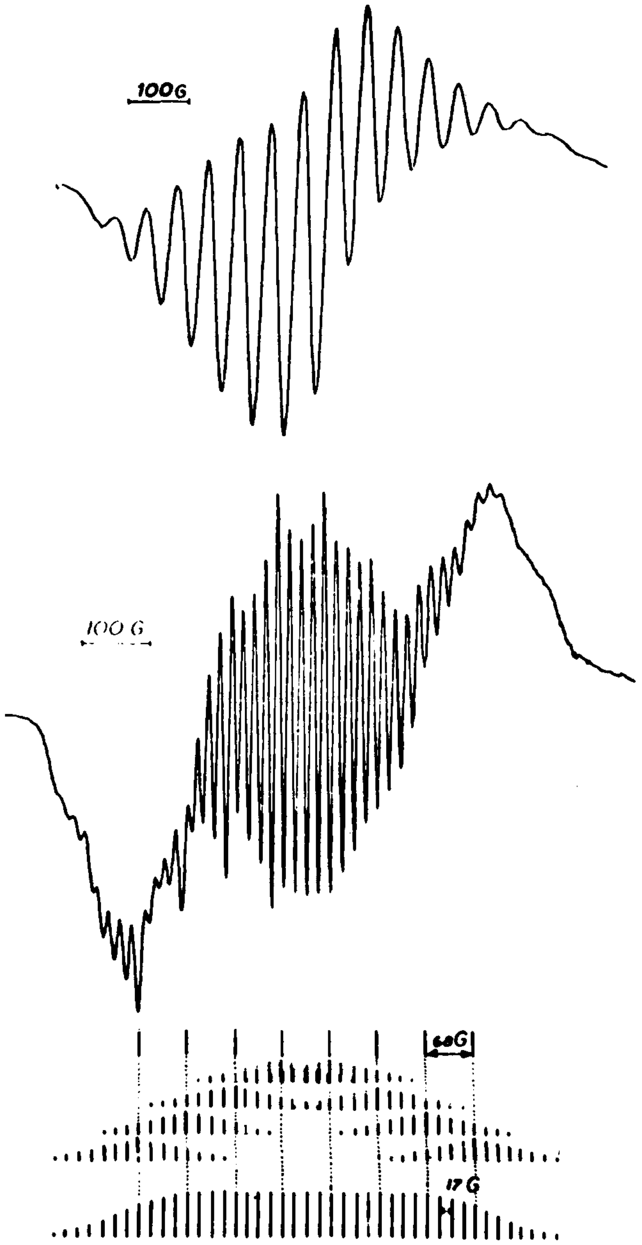

Figure 2. X-band ESR spectra recorded in pH 5 acetate buffer. Upper spectrum, **1a** at room temperature. Lower spectrum, **2a** at 70 °C.

15 (with relative intensities 1:2:3...8....1, a_2 = 17 G). Since the splitting pattern is unchanged between 40 and 120 °C, we conclude that, at these temperatures, the electron is trapped on one vanadium atom but delocalized by about 17% on each of the other two.[6] We note that the weighted average of a_1 and a_2 is 33 G, the expected splitting if the electron were to interact equally with the three ^{51}V nuclei.

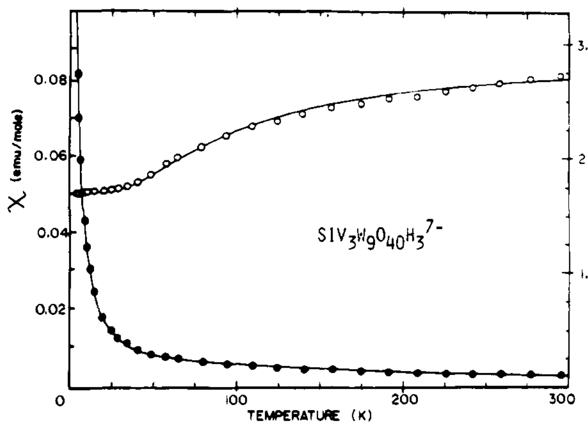

Figure 3. Temperature variation of magnetic susceptibility (●) and effective magnetic moment [$\mu_e = (7.997\chi T)^{1/2}$] (○) for $(K,Na)_7[SiV_3W_9O_{40}H_3]\cdot 12H_2O$. The curves drawn are the best fit of the data to the trimer equation as described in the text.

The inequivalence of the three vanadium nuclei in **2a** is considered to be the result of protonation at one of the V–O–W or V–O–V bridging oxygen atoms.[7] The ESR spectrum at pH >9 retained the same overall pattern of hyperfine lines superimposed on 8- and 15-line spectra. No spectrum was observed at pH 10.

Further reduction of **1a** and **2a** yields brown α-$SiV^{IV}_2W_{10}O_{40}^{8-}$ (**1b**) and α-$SiV^{IV}_3W_9O_{40}H_3^{7-}$ (**2b**) isolated as potassium salts. The electronic absorption spectra of these anions do not exhibit V(V)–V(IV) intervalence bands, observed at 9.0 × 10^3 and 9.7 × 10^3 cm^{-1} in the spectra of **1a** and **2a**, respectively. Susceptibility measurements[9] on the potassium salts reveal that there is essentially no magnetic exchange between the V(IV) atoms in **1b** (Curie–Weiss law behavior 109–4.3 K, θ = 0.5 ± 0.3 K, μ_{eff}/V = 1.71 μ_B). The magnetic data for **2b** are shown in Figure 3 and may be fitted to the standard expression for the susceptibility of an exchange-coupled trimer with three identical magnetic centers, $\chi = (Ng^2\beta^2/4kT)[1 + 5\exp(3J/kT)/1 + \exp(3J/kT)]$. The solid line in Figure 3 shows the fit obtained with $J = -34.9\ (\pm 0.5)$ cm^{-1}.

On the basis of the dimensions of Keggin structure tungstates and molybdates,[10] we estimate the separation between the vanadium atoms in **1** and **2** to be ~3.7 Å and the V═O (terminal) vectors to be canted away from each other by about 40°. The Unfavorable relaxation times which result in broad ESR spectra for **1b** and **2b** must result from the promixity and mutual orientation of the vanadium(IV) atoms.[11] The rather striking difference between the magnetic properties of **1b** and **2b** may be caused by protonation (V–O–V bridges in **1b**, V–O(H)–V in **2b**) and is the subject of further work.

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(6) The spectrum was unchanged when recorded in D_2O, or with sodium or ammonium counterions. The main features of the experimental spectrum were simulated by 43 gaussian lines with a mean line width of 18 G and relative intensities as deduced from the stick diagram.

(7) The p*K* values for $SiV_3W_9O_{40}H_2^{5-}$ are ca. 4.0 and 10.5. The reduced anion (**2a**) is thus expected to be singly protonated at pH 4.5–10. Details of the ESR spectra at different pHs and temperatures to 10 K will be discussed in a later paper.

(8) As neat solids, **1b** and **2b** also show weak transitions corresponding to $|\Delta m_s|$ = 2 and 3.

(9) Magnetic measurements were made on a SQUID susceptometer at the University of Virginia. For measurement and calibration procedures, see: O'Connor, C. J.; Sinn, E.; Cucauskas, E. J.; Deaver, B. S., Jr. *Inorg. Chim. Acta* **1979**, *32*, 29.

(10) Brown, G. M.; Noe-Spirlet, M. R.; Busing, W. R.; Levy, H. A. *Acta Crystallogr., Sect. B* **1977**, *B33*, 1038. Kobayashi, A.; Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 885. Allmann, R.; D'Amour, H. *Z. Kristallogr.* **1975**, *141*, 161.

(11) In contrast, well-resolved triplet-state ESR spectra are observed for oxovanadium tartrate dimers where V···V is ca 4.2 Å, but the relative orientation of the V═O vectors is close to 180°; see, for example: Toy, A. D.; Smith, T. D.; Pilbrow, J. R. *Aust. J. Chem.* **1974**, *27*, 1.

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Retention of Ring Structure in Cyclopentane and Alkylcyclopentane Molecular Cations

Sir:

In recent ion cyclotron resonance investigations, it was found that the photodissociation spectrum of the $C_5H_{10}^+$ ion formed by electron-impact ionization of cyclopentane coincided with that of $1\text{-}C_5H_{10}^+$ or $2\text{-}C_5H_{10}^+$, and it was concluded that cyclopentane ions quantitatively undergo ring opening.[1,2] In fact, upper limits of $<10^{-9}$ s have been suggested for the lifetime of alkyl-substituted cycloalkane molecular ions with 3–5-membered rings on the basis of a collisional activation and field ionization kinetic study.[3]

On the other hand, in an earlier gas phase radiolysis study,[4] it was demonstrated that only 20% of the parent ions from cyclopentane undergo ring opening to give *trans*-2-pentene (63%) and *cis*-2-pentene (37%) at a pressure of 20 torr. Furthermore, liquid phase radiolysis experiments indicated complete retention of the cyclic structure.[5] Here we are reporting experimental evidence which demonstrates that the apparent conflict can be resolved if one accepts, as is the case for cyclopropane and cyclobutane,[6] that the degree of ring opening in cyclopentane and alkylcyclopentane ions reflects the internal energy content of the molecular ions following the ionization process.

All measurements were taken with the NBS high-pressure photoionization mass spectrometer[7] operated, unless otherwise noted, at 292 K. The basic experimental approach involved the investigation of competitive charge exchange reactions occurring in cyclopentane–additive or alkylcyclopentane–additive mixtures (all API samples) in order to establish the fractional yields of cyclic ions. The additives were chosen to satisfy the following relationship involving ionization potentials (IPs): IP(cyclopentane) $\gg$ IP(additive) $\gg$ IP(olefinic isomers). When these criteria are met, the cyclic ion will undergo charge exchange with the additive, but the acyclic isomers will not. An obvious additional requirement was that the neutral components must not participate in any other ion–molecule reactions with either the cyclic or the olefinic ions derived from the particular neutral cyclopentane or the charge-exchange product. For example, cyclohexane's IP (9.88 eV)[8] is substantially lower than that of cyclopentane (IP = 10.50 eV)[8] and above those of any of the isomeric pentenes ($\leq$9.52 eV).[9] In a typical experiment, the fractional yield of $C_5H_{10}^+$ ions [defined as $I_{C_5H_{10}^+}/(I_{C_5H_{10}^+} + I_{C_6H_{12}^+})$] in a cyclopentane–cyclohexane mixture would be determined as a function of pressure in order to define that fraction of the $C_5H_{10}^+$ ions which did charge exchange with cyclohexane, i.e., that fraction which remained cyclic after ionization. Such data for two cyclopentane–cyclohexane mixtures following photoionization at 10.62 (curve A) and 11.7 eV (curve B) are given in Figure 1. Note that there are two regimes of essentially constant values for the fractional yields, at very low pressures in the reaction chamber, where collisions between $C_5H_{10}^+$ and cyclohexane are negligible, and at high pressures, where all of the cyclic $C_5H_{10}^+$ ions have reacted via charge exchange. The remaining fractional yield at higher pressures corresponds to the olefinic ions, which are unreactive toward cyclohexane. Consideration of the data from mixtures of various composition (2.5–10% cyclohexane) indicates that only 30 ± 2% of the $C_5H_{10}^+$ ions produced in the 11.7-eV photoionization of cyclopentane retain the cyclic structure contrasted with $\geq$96% of those formed at 10.62 eV. Charge exchange involving internally excited pentene ions and cyclohexane can be ruled out since, if this were the case, one would expect a higher probability for this process in the 11.7-eV photoionization (higher degree of internal excitation). As just mentioned, the opposite is true; i.e., only 30% of the $C_5H_{10}^+$ ions actually charge exchange at this energy.

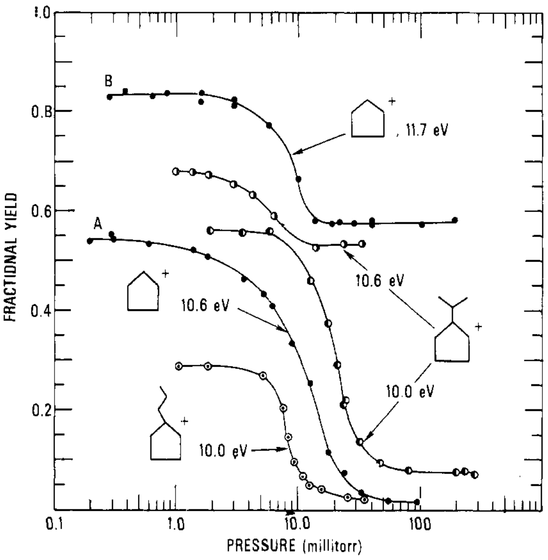

Figure 1. Fractional yields (see text for description) vs. total reaction chamber pressure. (A) Cyclopentane–cyclohexane (30:1), 10.6 eV; (B) cyclopentane–cyclohexane (10:1), 11.7 eV; (⊙) *n*-propylcyclopentane–*n*-propylcyclohexane (30:1), 10.0 eV, fractional yield/2 for clarity; (◑ and ◐) isopropylcyclopentane–isopropylcyclohexane (10:1), 10.6 and 10.0 eV, pressure scale shifted ×3 for clarity in 10.0-eV photoionization.

Four additional sets of measurements were performed at 10.62 eV. The effect of temperature on the extent of ring opening in cyclopentane was investigated in cyclopentane–cyclohexane mixtures. The results may be summarized as follows: (a) 292 K, >96% cyclic; 347 K, $\geq$94% cyclic; 386 K, 84 ± 4% cyclic; and 412 K, 78 ± 6% cyclic. (b) The equilibrium constant for the reaction $n\text{-}C_4H_{10}^+ + c\text{-}C_5H_{10} \leftrightarrow C_5H_{10}^+ + n\text{-}C_4H_{10}$ was determined from 292 to 348 K (increased decyclization precluded quantitative measurements above 348 K). A van't Hoff plot gives $\Delta H = -0.3$ kcal/mol, $\Delta S = +4.4$ eu, and $\Delta G_{300} = -1.6$ kcal/mol for the reaction as written.[10] With the IP of $n\text{-}C_4H_{10}$ as 10.50 eV,[8] a value of 10.49 eV is obtained for the IP of cyclopentane, in excellent agreement with the recommended value of 10.50 eV[8] obtained by photoionization/photoelectron spectroscopy. The addition of small quantities of cyclohexane as a charge acceptor to $n\text{-}C_4H_{10}$–cyclopentane mixtures removed $\geq$98% of the $C_5H_{10}^+$

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(10) A manuscript dealing with equilibrium measurements in a variety of alkanes and cycloalkanes will be submitted for publication shortly.