Inorg. Chem. **1989**, *28*, 3263-3264

Notes

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Improved Synthesis, Redox Chemistry, and Magnetism of the Mixed-Valence Isopolyanion $V_{10}O_{26}^{4-}$

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Received January 23, 1989

As part of our continuing studies of soluble oxo, alkoxide, and siloxide complexes as models for heterogeneous metal oxide catalysts,[1,2] we undertook the study of polyoxoanions because of their potential relevance[3] to the strong metal-support interaction (SMSI),[4] which is observed when mixed M'/MO_x catalysts (e.g., Rh/V_2O_5, Pt/TiO_2) are partially reduced under H_2. In particular, $V_{10}O_{26}^{4-}$, a mixed-valence isopolyvanadate,[5] was intriguing as a potential analogue of partially reduced V_2O_5. Published procedures[5a,6] for the synthesis of this anion proved impractical or irreproducible in our hands. We report here a reliable synthesis of $(^nBu_4N)_4V_{10}O_{26}$ in moderate yield from readily available starting materials. We also report a study of some of the physicochemical properties of this unusual isopolyvanadate, including a full temperature magnetic susceptibility study.

Experimental Section

General Considerations. Solvents were of reagent grade, except where noted, and were normally used without further purification. Acetonitrile used in electrochemical experiments was dried by distillation from CaH_2. V_2O_5 was either obtained commercially (Fisher Certified) or prepared via pyrolysis of NH_4VO_3 in air at 400 °C for 10 h.[7] All other reagents were commercially available.

Electrochemical measurements were performed in a Vacuum Atmospheres glovebox by using a Soltec Model VP-6423S X-Y recorder and BAS Model CV-27 potentiostat. A reference electrode consisting of a cracked-glass-bead outer shell (Fisher) containing a silver wire in a saturated $AgCl/Me_4N^+Cl^-$ CH_3CN solution was used. The potential of the Cp_2Fe/Cp_2Fe^+ couple vs this reference was +0.89 V with typical $\Delta E_p \sim$ 80–90 mV. Cyclic voltammograms were recorded in a single-compartment cell with 0.1 M $^nBu_4NBF_4$ by using a 0.03-in. Pt-disk working electrode; a 0.03-in. platinum wire served as the auxiliary electrode.

Infrared spectra were obtained on a Mattson Alpha Centauri FT-IR spectrophotometer. Magnetic susceptibility measurements (10–290 K) were made by using a Faraday balance; corrections for diamagnetism were estimated from Pascal's constants.[8] Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

$(^nBu_4N)_4V_{10}O_{26}$ (1). To a rapidly stirred slurry of V_2O_5 (4.00 g, 22.0 mmol) in 300 mL of technical acetone was added 112 mL of 10% aqueous $^nBu_4NOH$ solution (11.2 g, 43.2 mmol). This mixture was stirred at room temperature for 5–10 min, and then $VOSO_4{\cdot}xH_2O$ (2.3 g, 10.6 mmol based on $x = 3$) was added with vigorous stirring. Within 1 min, the solution turned deep purple. The solution was stirred 20 min and filtered through a pad of Celite to remove unreacted V_2O_5, and the pad was washed with ca. 150 mL of CH_2Cl_2. The organic layer was then separated, washed with 2 × 100 mL of water, and dried over anhydrous $MgSO_4$. The resulting solution was concentrated under reduced pressure to 20 mL and deposited small purple needles, which were collected by filtration, washed with diethyl ether, and dried in vacuo. Further concentration of the filtrate and cooling to 0 °C yielded a second crop of purple needles. The total yield was 4.9 g (47%). An infrared spectrum (KBr) was identical with that reported in the literature.[6] Anal. Calcd for $C_{16}H_{36}N_4O_{26}V_{10}$: C, 40.56; H, 7.66; N, 2.96. Found: C, 40.73; H, 7.42; N, 2.99

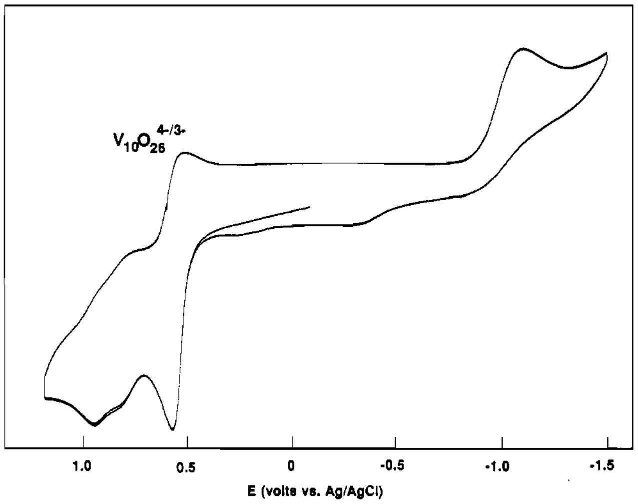

Figure 1. Cyclic voltammogram of 1.0 mM **1** in acetonitrile (0.1 M $^nBu_4N^+BF_4^-$ supporting electrolyte, scan rate 200 mV/s) referenced to Ag/AgCl ($E(Cp_2Fe/Cp_2Fe^+ = 0.89$ V)). Cycling between 0.8 and 0.0 V confirmed the reversible nature of the oxidation at 0.61 V.

Results and Discussion

The addition of vanadyl(IV) ion to V_2O_5 and $^nBu_4NOH$ in aqueous acetone (eq 1) provided a convenient route to the mixed-valence compound $(^nBu_4N)_4V_{10}O_{26}$ (**1**) first reported by Heitner-Wirguin and Selbin.[5a] Its unusual wheellike structure, containing two $V^{IV}O_5$ square pyramids and eight V^VO_4 tetrahedra, was later determined by Bino et al.[5b]

$$4V_2O_5 + 2VOSO_4 + 8^nBu_4NOH \xrightarrow{\text{acetone}/H_2O} (^nBu_4N)_4V_{10}O_{26} + 2(^nBu_4N)_2SO_4 + 4H_2O \quad (1)$$

Cyclic voltammetry of **1** in acetonitrile (see Figure 1) showed an irreversible reduction at −1.25 V and a reversible oxidation wave ($\Delta E_p \sim$ 80 mV) at −0.61 V (vs Ag/AgCl). The oxidation displayed a linear i vs $v^{1/2}$ response for scan rates from 50 to 300 mV/s. At more positive potentials, a number of irreversible oxidations were seen. In spite of the reversible nature of the first oxidation, presumably to give $V_{10}O_{26}^{3-}$, we were unable to effect the oxidation with a variety of chemical oxidants. Reaction with ferrocenium ion, I_2, and 7,7,8,8-tetracyanoquinodimethane (TCNQ) all resulted in the same green mixture of compounds. Even a controlled-potential bulk electrolysis of a solution of **1**

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(7) Use of commercial V_2O_5 resulted in slightly lower yields.

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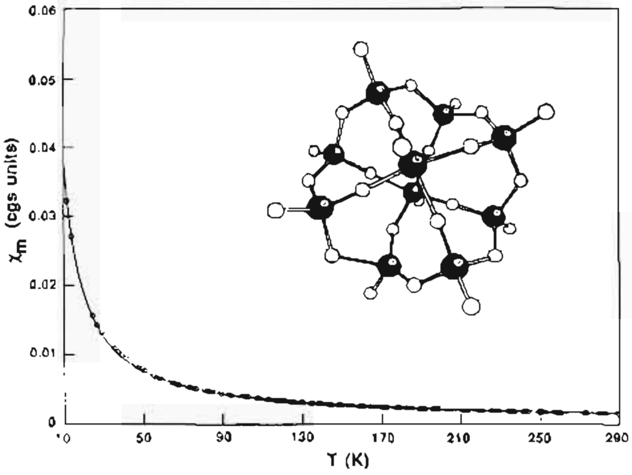

Figure 2. Plot of molar susceptibility for **1** from 10 to 290 K. The open circles are data; the line is the best fit to the Van Vleck equation (see text). Also shown is the structure of the $V_{10}O_{26}{}^{4-}$ ion (V^{IV}–V^{IV} = 4.44 Å).[4b]

decomposed the cluster to give the same uncharacterizable mixture. This behavior was somewhat unexpected, considering that many polyoxoanion structures are stable to oxidation or reduction.[9] It is interesting to note that the well-known[10] $H_3V_{10}O_{28}{}^{3-}$ displays irreversible reduction chemistry, at least in acetonitrile solution.

The solution ESR spectrum of $V_{10}O_{26}{}^{4-}$ reported by Heitner-Wirguin and Selbin shows a 15-line pattern with $a(^{51}V) = 102$ G, consistent with coupling to two equivalent ^{51}V nuclei ($I = {}^7/_2$). In order for two d^1 centers to give rise to this type of pattern, the coupling between the triplet and singlet electronic states must be at least a great as the hyperfine coupling in the ESR spectrum (~0.01 cm^{-1} at 9.5 GHz).[11] With this in mind, we undertook a thorough investigation of the magnetic properties of the compound. Figure 2 shows data for corrected molar susceptibility ($\chi_m{}^{cor}$) as a function of temperature; superimposed is the best-fit curve for the susceptibility derived from the Van Vleck equation (eq 2),[12] which assumes an interaction of the form $\mathcal{H} = -2J\mathbf{S}_1\cdot\mathbf{S}_2$.

$$\chi = \frac{N_g{}^2\beta^2}{3kT}\left[1 + \frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right] + \mathrm{TIP} \tag{2}$$

The compound has $\mu_{eff} = 1.85\ \mu_B$[13] per V^{IV} center at 293 K, perhaps suggestive of ferromagnetic coupling. The curve shown is for $2J = 0.9\ cm^{-1}$, indicating a weak ferromagnetic coupling (i.e., triplet ground state), which is ~100 times greater than the coupling necessary to rationalize the ESR spectrum. The temperature-independent paramagnetism (TIP) is estimated to be ~3 × 10^{-4} cgsu/mol, considered normal for a first-row complex.[14] Dimeric vanadyl(IV) tartrate complexes, which are structurally similar to $V_{10}O_{26}{}^{4-}$, also display ferromagnetic coupling;[15] however, the quality of the published data is not sufficient to allow for meaningful comparisons. To date, these are the only known ferromagnetically coupled vanadyl complexes.[16]

Acknowledgment. The authors wish to thank the Air Force Office of Scientific Research and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. S.M.B. acknowledges the Shell Companies Foundation for fellowship support.

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(16) One reviewer brought to our attention an example of ferromagnetically coupled V^{IV} atoms in the heteropolyanion $[\alpha\text{-}1,2,3\text{-}SiV^{IV}{}_3W_9O_{40}H_3]^{7-}$: Mossoba, M. M.; O'Connor, C. J.; Pope, M. T.; Sinn, E.; Hervé, G.; Tézé, A. *J. Am. Chem. Soc.* **1980**, *102*, 6864–6866. In this compound, the V^{IV} atoms are estimated to be separated by ~3.7 Å in adjacent corner-sharing octahedral sites of a Keggin structure. The magnitude of the ferromagnetic coupling was found to be $J = 34.9\ cm^{-1}$, but interestingly, no magnetic interaction was found in the disubstituted analogue $[\alpha\text{-}1,2\text{-}SiV^{IV}{}_2W_{10}O_{40}]^{8-}$

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Influence of Remote Substituents on the Properties of Bis(terpyridyl)ruthenium(II) Complexes

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Received June 1, 1988

In recent years considerable effort has been expended in trying to better understand the chemistry of ruthenium(II) diimine complexes. Much of this work has been directed toward the ultimate realization of an effective photoredox catalyst.[1] Two features that are important in the development of such a species are the absorption of light of useful wavelength and the existence of a sufficiently long-lived excited state to allow electron transfer to compete favorably with internal return to the ground state. In the area of $Ru(bpy)_3{}^{2+}$ chemistry (bpy = 2,2′-bipyridine), the primary design emphasis has focused on variation of the electronic and steric properties of the ligands to help control and modify the properties of their complexes.[2]

A ligand very closely related to bpy, which coordinates readily with ruthenium(II) in a 2:1 fashion, is 2,2′:6′,2″-terpyridine (tpy).[3] $Ru(tpy)_2{}^{2+}$ has been less widely studied primarily because its room-temperature excited-state lifetime is much shorter than that of $Ru(bpy)_3{}^{2+}$, although the underlying reasons for this are not clearly understood.[4] Nevertheless, tpy complexes are of fundamental interest for several reasons. These complexes exhibit a symmetry different from that of analogous bpy complexes. Substitution at the 4′-position of tpy does not alter the symmetry of a $Ru(tpy)_2{}^{2+}$ complex, while monosubstitution on a bpy ligand

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