Derivatives of Tetrathiovanadate(V): Synthesis of the Linear Heterometallic Fe(μ_2-S)$_2$V(μ_2-S)$_2$Fe Core and the Structures of [VS$_4$]$^{3-}$ and [VFe$_2$S$_4$Cl$_4$]$^{3-}$

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Received July 18, 1983

The well-explored chemistry of the group 6a tetrathiometalates [MS$_4$]$^{2-}$ (M = Mo, W) has included, inter alia, use of these dianions as precursors to heterometallic complexes containing the fundamental "linear" FeS$_2$M, FeS$_2$MS$_2$Fe, and MS$_2$FeS$_2$M[1,2] and the cubane-like MFe$_3$S$_4$[3] core structural units. Development of group 5a tetrathiometalate(V) chemistry is hampered in part by the intractability of [M'(I)]$_3$MS$_4$,[4] the only known forms of the M = Nb, Ta trianions. However, the venerable compound (NH$_4$)$_3$VS$_4$[5] is water soluble, albeit extremely hydrolytically sensitive. Early crystallographic results[6] indicated an unexpectedly large range of V–S distances (2.09–2.18 Å) compared to Mo–S distances in (NH$_4$)$_2$MoS$_4$[7] (mean 2.178 (6) Å), prompting a structural redetermination.[8] The structure of [VS$_4$]$^{3-}$ (Figure 1) has imposed C_s symmetry. Deviations from T_d symmetry are evident but, in terms of bond distances, are substantially smaller than those reported earlier.[6] The derivative chemistry of highly basic [VS$_4$]$^{3-}$, previously unexplored, has been examined.

Anaerobic reaction of R$_4$N$^+$ salts (R = Me, Et) of [FeCl$_4$]$^{2-}$[9] and [Fe(SPh)$_4$]$^{2-}$[10,11] or [Fe$_4$(SPh)$_{10}$]$^{2-}$[11] in acetonitrile solution with solid (NH$_4$)$_3$VS$_4$ (Fe:V = 2:1) gave intense red solutions. Recrystallization (acetonitrile–ether or DMF–ether) of the solids obtained by addition of ether to reaction mixture filtrates afforded analytically pure, red-black crystalline salts of [VFe$_2$S$_4$X$_4$]$^{3-}$ (X = Cl (1), SPh (2)): (R$_4$N)$_3$-1,[12a] 45–58%; (R$_4$N)$_3$-2,[12b] 42–66%. Similar reaction systems with [MCl$_4$]$^{2-}$ (M = Mn(II), Co(II), Ni(II)) yielded insoluble black precipitates. Absorption spectra of 1 and 2 in acetonitrile[12] revealed the presence of a perturbed [VS$_4$]$^{3-}$ chromophore (λ_{max} 351, 394, 538 nm for [VS$_4$]$^{3-}$ in aqueous alkaline solution[13]), whose nature was established by structure determination of (Me$_4$N)$_3$-1·DMF.[8a,14] The structure of 1 (Figure 2) contains a nearly linear FeS$_2$VS$_2$Fe core (Fe–

Figure 1. Structure of [VS$_4$]$^{3-}$ as its NH$_4^+$ salt; esd values of distances and angles are 0.001 Å and <0.1°, respectively. Atoms S(3) and S(3') are related by a mirror plane; atoms are shown with 50% probability ellipsoids.

Figure 2. Structure of [VFe$_2$S$_4$Cl$_4$]$^{3-}$ (1) showing mean values of distances and angles under idealized D_{2d} symmetry and 50% probability ellipsoids. Values or ranges of interatomic distances (Å): V–Fe(1), 2.737 (2); V–Fe(2), 2.723 (2); V–S, 2.171 (2)–2.184 (2); Fe–S, 2.265 (3)–2.283 (3); Fe–Cl, 2.265 (3)–2.276 (3).

(1)–V–Fe(2) 172.9 (1)°) incorporated in three edge-shared tetrahedra whose overall symmetry approaches D_{2d}. The two FeS$_2$V subunits are not quite planar, atom deviations from least-squares planes being ±(0.05–0.06) Å; the dihedral angle between the planes is 89.2°. The mean V–S distance is elongated by 0.02 Å compared to [VS$_4$]$^{3-}$ as a consequence of binding the two FeCl$_2$ groups. The magnetic moment μ_{Fe} = 4.96 μ_B (solid, 299 K) and the mean Fe–Cl distance of 2.270 (5) Å[15] support the formulation 2Fe(II) + V(V).

The configuration of 1 is precedented by the near-D_{2d} stereochemistry of valence-isoelectronic [MoFe$_2$S$_4$Cl$_4$]$^{2-}$[16] (3); however, there are structural and other property differences of significance. Mean Fe–S and Fe–Cl distances in 1 are 0.02 Å shorter and nearly 0.05 Å longer, respectively, than the values for 3. Electronic spectra of 1 in solvents of different coordinating ability (nitromethane, acetonitrile, DMF) are nearly identical, indicating structural integrity in solution. Treatment of 1 in acetonitrile with excess (Et$_4$N)(SPh) affords a species whose chromophore[12b] and ^{1}H NMR spectrum (meta H 32.7 ppm downfield, ortho H 23.4 ppm and para H 29.9 ppm upfield of Me$_4$Si reference, 303 K) are identical with those of isolated (R$_4$N)$_3$-2. The composition of the latter and other properties, including μ_{Fe} = 4.80 μ_B (solid, 299 K), indicate that 2 has the FeS$_2$VS$_2$Fe core of 1. The absence of any other NMR signals demonstrates that 1 undergoes terminal ligand substitution only; i.e., it is not cleaved to the potential products [(PhS)$_2$FeS$_2$VS$_2$]$^{3-}$ and [Fe(SPh)$_{4-n}$Cl$_n$]$^{2-}$. In contrast, 3 in DMF is extensively dissociated in the reaction [MoFe$_2$S$_4$Cl$_4$]$^{2-}$

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(8) (a) Diffraction data were collected at ambient temperature on a Nicolet R3m instrument using monochromatized Mo Kα radiation. Structures were solved by a combination of direct methods and subsequent difference Fourier maps; absorption corrections were applied. (b) (NH$_4$)$_3$VS$_4$: a = 9.432 (2) Å, b = 10.825 (2) Å, c = 9.309 (2) Å; space group, *Pnma*; Z = 4; d_{calcd} (d_{obsd}) = 1.63 (1.65) g/cm^3; 1423 unique data ($I > 3\sigma(I)$); R (R_w) = 2.6 (2.9)%.

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(12) (a) Anal. Calcd for (Et$_4$N)$_3$-1 (Found): C, 35.01 (34.67); H, 7.34 (7.28); Cl, 17.22 (17.63); Fe, 13.56 (13.50); N, 5.10 (5.35); S, 15.57 (15.67); V, 6.19 (6.43). Absorption spectrum (acetonitrile) λ_{max} 232 (ϵ_M 32 100), 250 (sh), 310 (12 600), 350 (sh), 396 (5500), 516 (6400), 700 (sh). (b) Anal. Calcd for (Et$_4$N)$_3$-2 (Found): C, 51.55 (50.78); H, 7.21 (7.14); Fe, 9.99 (9.94); N, 3.76 (3.82); S 22.94 (22.55); V, 4.56 (4.54). Absorption spectrum (acetonitrile) λ_{max} 241 (ϵ_M 48 600), 268 (45 400), 296 (sh), 340 (sh), 428 (15 100), 533 (11 400), 572 (sh).

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(14) (Me$_4$N)$_3$-1·DMF: a = 16.058 (3) Å, b = 11.371 (2) Å, c = 19.856 (4) Å, β = 110.20 (1)°; space group, $P2_1/c$; Z = 4, d_{calcd} (d_{obsd}) = 1.42 (1.42) g/cm^3; unique data ($I > 3\sigma(I)$), 3540; R (R_w) = 5.0 (5.6)%. All non-hydrogen atoms except those of the uncoordinated, disordered DMF molecule were refined anisotropically. Crystals were obtained by vapor diffusion of ether into a DMF solution.

(15) Mean Fe–Cl distances: [FeCl$_4$]$^{2-}$, 2.292 (2) Å (Lauher, J. W.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 348); [FeCl$_4$]$^{1-}$, 2.185 (2) Å (Kistenmacher, T. J.; Stucky, G. D. *Ibid.* **1968**, *7*, 2150).

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$\rightleftharpoons [Cl_2FeS_2MoS_2]^{2-}$ (**4**) + $FeCl_2$.[16] Reaction of well-authenticated **4**[16-18] with PhS⁻ affords $[(PhS)_2FeS_2MoS_2]^{2-}$[17] (**5**), also obtainable by other methods.[16-19] As yet we have found no routes to the vanadium analogues of binuclear **4** and **5** or to the molybdenum analogue of trinuclear **2**.

The foregoing structural and reactivity differences of $[MoS_4]^{2-}$ and $[VS_4]^{3-}$—notably the large difference in Fe–Cl bond lengths between **1** and **3** and the ready formation and stability of *tri*nuclear **1** and **2**—are particularly clear manifestations of the higher negative charge of $[VS_4]^{3-}$ and attendant enhanced affinity for binding of FeX_2 groups with either hard (X = Cl) or soft (X = SPh) ligands. Highly stable interactions of these sorts are not sustained by $[MoS_4]^{2-}$. This feature may permit synthesis of extended linear metal–sulfur arrays on the basis of repeating $[VS_4]^{3-}$ units, a matter under investigation. One further problem in group 5a thiometalate chemistry is the preparation of discrete Nb(V) and Ta(V) ions. We have been unable to repeat the reported synthesis of $[NbO_2S_2]^{3-}$.[20] However, syntheses of soluble salts of $[M_6S_{17}]^{4-}$ (M = Nb, Ta), ions with exceptional structures, have been developed.[21] This research and a more detailed account of Fe–V–S chemistry will be presented subsequently.

Supplementary Material Available: X-ray structural data for $(NH_4)_3VS_4$ and $(Me_4N)_3[VFe_2S_4Cl_4]\cdot DMF$: positional and isotropic and anisotropic thermal parameters (4 pages). Ordering information is given on any current masthead page.

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Nitroxyl-Mediated Electrooxidation of Amines to Nitriles and Carbonyl Compounds

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Received August 2, 1983

Oxidations employing an electrochemically regenerated reagent are finding increasing application in organic synthesis.[1] We have been interested in the oxidizing and other chemical properties of the nitrosonium ion **1**, which is easily generated by electrooxidation of 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO, **2**) at + 0.33 V (vs. Ag/Ag⁺).[2] The oxidation of alcohols to aldehydes and ketones using catalytic amounts of **2** and controlled potential electrolysis has been reported, including the observation of a special selectivity for primary alcohols in the presence of secondary al-

(1) Shono, T. *Tetrahedron Lett.* **1979**, 3861–3864. Shono, T.; Matsumura, Y. Hayashi, J. *Ibid.* **1980**, 1867–1870. Shono, T.; Matsumura, Y.; Hayashi, J.; Mizoguchi, M. *Ibid.* **1979**, 164–168. Leonard, J. E.; Scholl, P. C.; Steckel, T. P.; Lentsch, S. E.; van der Mark, M. R. *Ibid.* **1980**, 4695–4699. Yoshida, J.-i.; Nakai, R. N. *J. Org. Chem.* **1980**, *45*, 5269.

(2) Cation **1** is easily formed by oxidation of the readily available nitroxy **2** with (a) chlorine (Golubev, V. A.; Rozantsev, E. G.; Neiman, M. B. *Bull. Akad. Sci. USSR* **1965**, 1927–1936), (b) peracid (Cella, J. A.; Kelley, J. A.; Kenehan, E. F. *Tetrahedron Lett.* **1975**, 2869–2872), and (c) electrooxidation (Sümmermann, W.; Deffner, U. *Tetrahedron* **1975**, *31*, 593–596).

Scheme I
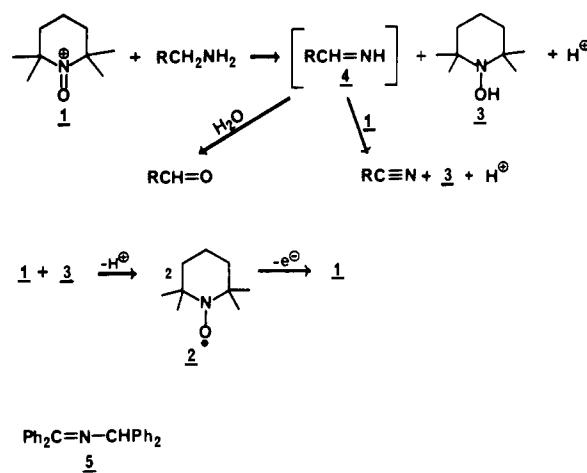
cohols.[3,4] Here we report the reactions of amines under similar oxidation conditions, demonstrating efficient direct formation of aldehydes and ketones (in aqueous media) and a direct conversion to nitriles (in anhydrous acetonitrile).[5-7]

In the process (Scheme I), the nitrosonium ion **1** is expected to react with the amine, eliminating a proton and producing the hydroxylamine **3**.[8] Syn proportionation of **1** and **3** produces **2**, which is reoxidized electrochemically to complete a catalytic cycle. A weak base (2,6-lutidine is satisfactory) is used to avoid the inhibiting effect of high acid concentration. Imines (**4**) are the expected intermediates, which can react again with **1** to produce nitriles or can be hydrolyzed to carbonyl compounds; imines have not been detected.

Reactions are performed at 23 °C and are generally complete in a few hours using initial currents in the range 200–300 mA. The amount of catalyst at the start (0.2–0.4 mol equiv) is adjusted to provide complete conversion and reasonable rates, as the nitrosonium ion **1** slowly decomposes during the oxidation. The reactions proceed with about 90% Coulomb efficiency on the basis of starting amine. In the simplest procedure (A), the amine (1 mmol), 2,6-lutidine (8 mmol), and **2** (0.2 mmol; or the 4-hydroxy analogue[9]) were added to 25 mL of electrolyte solution[10] in a

(3) Electrocatalytic oxidation of alcohols and special selectivity were reported very recently: Semmelhack, M. F.; Chou, C. S.; Cortès, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 4492.

(4) The first observation of oxidation of alcohols with **1** (generated chemically) demonstrated simply that methyl, ethyl, and isopropyl alcohols could be converted into the corresponding carbonyl compounds: (a) Golubev, V. A.; Rozantsev, E. G.; Neiman, M. B. *Bull. Akad. Sci. USSR* **1978**, 1874–1881. A combination of **2** and peracid is also reported to convert alcohols to aldehydes (and acids) and ketones: (b) Cella, J. A.; Kelley, J. A.; Kenehan, E. F. *J. Org. Chem.* **1975**, *40*, 1860–1862. (c) Ganem, B. *Ibid.* **1975**, *40*, 1998–1999.

(5) Highly electrophilic oxidizing agents of the sort that readily oxidize alcohols have not been generally successful in the conversion of amines to carbonyl compounds. For examples and discussion, see: (a) Rawalay, S. S.; Schechter, H. *J. Org. Chem.* **1967**, *32*, 3129. (b) Audette, R. J.; Quail, J. W.; Smith, P. J. *Tetrahedron Lett.* **1971**, 279. (c) Stephens, F. F.; Bower, J. D. *J. Chem. Soc.* **1949**, 2971. Nakagawa K.; Onoue, H. Sugita, J. *J. Chem. Pharm. Bull.* **1964**, *12*, 1135.

(6) Direct methods for converting amines to nitriles with electrophilic reagents are rare. For examples, see: (a) Kametani, T.; Takahashi, K.; Ohsawa, T.; Ihara, M. *Synthesis* **1977**, 245. (b) Schmidt, H.-J.; Schäfer, H. J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 109. (c) Czarny, M. *Synth. Commun.* **1976**, *6*, 285. Recently, a direct electrochemical method employing nickel hydroxide electrodes in a basic medium has been reported for conversion of simple amines to nitriles. It is not useful for conversion of amines to aldehydes: (d) Fledhues, U.; Schäfer, H. J. *Synthesis* **1982**, 145–146.

(7) An indirect strategy for conversion of amines to ketones and aldehydes is based on a biological process and is not applicable for the formation of nitriles. The practical examples of the biomimetic scheme require several operations and fairly complex reagents in stoichiometric amounts but can give high efficiency. For a brief review of amine oxidation and leading references, see: Buckley, T. H.; Rappoport, H. *J. Am. Chem. Soc.* **1982**, *104*, 4446.

(8) Hydroxylamine **3** has not been detected in the amine oxidations, but it was characterized in the study of alcohol oxidations[3] and is a reasonable product from amines as well.