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Tetrathiovanadate(V) and Tetrathiorhenate(VII): Structures and Reactions, Including Characterization of the VFe_2S_4 Core Unit

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The structural and derivative chemistry of $[VS_4]^{3-}$ and $[ReS_4]^-$ has been investigated. $(NH_4)_3[VS_4]$ crystallizes in orthorhombic space group *Pnma* with $a = 9.432$ (2) Å, $b = 10.825$ (2) Å, $c = 9.309$ (2) Å, and $Z = 4$. With use of 1423 unique data ($I > 3\sigma(I)$) the structure was refined to $R = 2.6\%$. $(n\text{-}Bu_4N)[ReS_4]$ occurs in orthorhombic space group *Pcnn* with $a = 11.355$ (2) Å, $b = 11.334$ (2) Å, $c = 18.566$ (2) Å, and $Z = 4$. The structure was refined to $R = 4.1\%$ on the basis of 1222 unique data ($I > 3\sigma(I)$). Both ions are slightly distorted tetrahedra with the mean bond lengths V–S = 2.154 (16) Å and Re–S = 2.123 (5) Å. The ^{187}Re resonance of $[ReS_4]^-$ occurs at 2586 ppm downfield of $[ReO_4]^-$ in acetonitrile at 297 K. The reaction system $(NH_4)_3[VS_4]/FeCl_2$ in acetonitrile affords the trinuclear cluster $[VFe_2S_4Cl_4]^{3-}$ (**1**) in good yield. $(Me_4N)_3[VFe_2S_4Cl_4]\cdot DMF$ crystallizes in monoclinic space group $P2_1/c$ with $a = 16.058$ (3) Å, $b = 11.371$ (2) Å, $c = 19.856$ (4) Å, $\beta = 110.20$ (1)°, and $Z = 4$. The structure was refined to $R = 5.0\%$, with use of 3540 unique data ($I > 3\sigma(I)$). The anion contains a new structural unit, the nearly linear $[Fe(\mu\text{-}S)_2V(\mu\text{-}S)_2Fe]^+$ core (Fe–V–Fe = 172.9 (1)°), and is formed from three edge-shared tetrahedra. The overall symmetry of $[VFe_2S_4Cl_4]^{3-}$ closely approaches D_{2d}; the cluster is isostructural with $[MFe_2S_4Cl_4]^{2-}$ (M = Mo, W). Reaction of $(NH_4)_3[VS_4]$ with $[Fe(SPh)_4]^{2-}$ or $[Fe_4(SPh)_{10}]^{2-}$, or of $[VFe_2S_4Cl_4]^{3-}$ with PhS^-, yields $[VFe_2S_4(SPh)_4]^{3-}$ (**2**), which was isolated as R_4N^+ salts. Spectral and magnetic data indicate **1** and **2** contain the same core unit, with two high-spin Fe(II) atoms. In acetonitrile with equimolar $[Fe(SPh)_4]^{2-}$, $[ReS_4]^-$ is ~50% converted to $[(PhS)_2FeReS_4]^-$, which was detected by ^1H NMR but was not isolated. Reaction of $[VS_4]^{3-}$ and CuCN gave $[VS_4Cu_3(CN)_3]^{3-}$, isolated as its $n\text{-}Bu_4N^+$ salt; a structure is proposed. The set of tetrathiometalates $[MS_4]^{3-,2-,-}$ (M = V(V), Mo(VI), W(VI), Re(VII)) display structural and reactivity properties that are largely controlled by oxidation state and ion charge. The binding affinity order $[ReS_4]^- < [MoS_4]^{2-} \simeq [WS_4]^{2-} < [VS_4]^{3-}$ toward $FeCl_2$ in acetonitrile solution is a clear example of this behavior.

Introduction

The tetrathiometalates $[MS_4]^{z-}$ are the simplest members of a rapidly expanding class of transition-element compounds that we have termed "soluble metal sulfides".[1,2] The set contains d^0 ions and includes $[VS_4]^{3-}$, $[MoS_4]^{2-}$, $[WS_4]^{2-}$, and $[ReS_4]^-$, which are the terminal members of the series $[MO_{4-n}S_n]^{z-}$, obtained by the reaction of H_2S with, initially, polyoxometalates in aqueous alkaline solution. Tetrathiometalates are intense UV/visible chromophores and have been isolated as discrete ions in simple salts. Their syntheses and properties have been usefully summarized.[3] The chemistry of $[MoS_4]^{2-}$ and $[WS_4]^{2-}$ is by far the most highly developed. Of particular importance is their utility as precursors to linear and cubane-type MFe_3S_4 clusters,[3-7] some of which (M = Mo) are relevant to the native Mo–Fe–S cluster of nitrogenase.[4-7]

Of the other conceivable and known transition-element tetrathiometalates, it has been argued that $[CrS_4]^{2-}$ and $[MnS_4]^-$ are too unstable to exist,[8] a position consistent with our experience. Attempts to prepare $[MS_4]^{3-}$ (M = Nb, Ta) as discrete ions have thus far led to the polynuclear cage anions $[M_6S_{17}]^{4-}$.[1] In the reaction of $[TcO_4]^-$ and H_2S in aqueous solution, some $[TcO_3S]^{2-}$ may have been formed,[8] but no $[TcS_4]^-$ was detected. There being no evidence whatever for the formation of $[MS_4]^{z-}$ past group 7, this leaves $[VS_4]^{3-}$ and $[ReS_4]^-$ as the remaining accessible tetrathiometalates. Although $[VS_4]^{3-}$ was first prepared in 1890[9] and $[ReS_4]^-$ in 1931,[10] the species have not been extensively investigated, and virtually nothing is known of their reaction chemistry. Prior work has been confined to electronic and vibrational spectroscopy[3,8,11-13] and several X-ray diffraction experiments.[14,15] Here we elaborate our earlier report of the derivative chemistry of $[VS_4]^{3-}$,[16] including accurate structures of the ion and $[ReS_4]^-$, their reactions with Fe(II), and characterization of a new structural unit, the nearly linear VFe_2S_4 core.

Experimental Section

Preparation of Compounds. All operations were performed under a pure argon or dinitrogen atmosphere unless otherwise noted. Solvents were purified by distillation from suitable drying agents. The compounds NH_4VO_3, $NaReO_4$, and Re_2O_7 (Alfa), 40% NH_4OH, CuCN, and NaCN (Fisher), R_4NX (R = *n*-Bu, Et, Me; X = Br, Cl) (Aldrich), and H_2S (Matheson) were used as received. $(R_4N)_2[FeCl_4]$,[17] $(R_4N)_2[Fe_4(SPh)_{10}]$[18] (R = Me, Et), and $(Et_4N)_2[Fe(SPh)_4]$[18,19] were prepared as described elsewhere.

$(NH_4)_3[VS_4]$. The following modified version of the reported procedure[9] was used to prepare this compound with high purity, free from contaminants with ν_{VO} around 900 cm^{-1} in the IR spectrum. A stream of H_2S gas was passed at a medium rate through an ice-cooled solution of 10 g of NH_4VO_3 in 1 L of 40% NH_4OH. The solution initially turned to yellow and then orange. After 10–15 min a light brown precipitate appeared and redissolved. The solution then underwent sequential color changes to brown, red, and finally to violet after H_2S was passed for 3–4 h. At this stage microcrystalline material could be observed. H_2S was allowed to bubble through for at least 8 h from the beginning of the experiment. A dark violet crystalline solid was collected, washed well

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with absolute ethanol and ether, and dried in vacuo; 4.1 g of product as the first crop was obtained. A second crop of product could be obtained upon passage of H_2S through the filtrate and storage at ~4 °C. X-ray diffraction quality single crystals were grown by slow cooling of this filtrate. IR spectrum (KBr): 478 cm^{-1} (ν_{VS}). Absorption spectrum (1.0 M aqueous NaOH solution): λ_{max} 544 (ϵ_M 3800), 394 (2700), 349 (3700), 265 (9100) nm.

(n-Bu$_4$N)[ReO$_4$]. To a solution of 2.03 g (7.43 mmol) of $NaReO_4$ in ~40 mL of H_2O was added aerobically a solution of 3.60 g (11.2 mmol) of n-Bu_4NBr in an equal volume of H_2O. A flocculent white solid formed immediately and was collected by filtration after the reaction mixture was stirred for 30 min at room temperature. This material was washed with H_2O and ether and dried in vacuo; 3.16 g (86%) of product was obtained. IR spectrum (KBr): 906 cm^{-1} (ν_{ReO}). ^{187}Re NMR spectrum (acetonitrile): 0 ppm ($\Delta_{1/2} \simeq$ 3030 Hz).

(n-Bu$_4$N)[ReS$_4$]. The following description is similar to a reported method[12a] but is more explicit. Re_2O_7 (2.0 g, 4.1 mmol) was dissolved in 2 L of 40% NH_4OH solution. Initially, a violent exothermic process took place with formation of a black solid that slowly redissolved to give a clear solution. The reaction mixture was heated slightly, and a stream of H_2S was introduced. No color change was observed during the first ~15 min. Thereafter, the solution changed sequentially to yellow, orange, red, and violet with the formation of a black precipitate. At this point the H_2S stream was discontinued and 20 g of KOH was added, causing effervescence. The contents were heated to boiling (10 min) and filtered while hot into an aqueous solution of excess n-Bu_4NCl. The red-purple flocculent material was collected in the air, washed with 10:1 v/v ether/methanol, and dried with a water aspirator. Recrystallization from acetonitrile afforded black needle-shaped crystals, which were collected, washed with ether, and dried in vacuo; 0.88 g (20%) of pure product was obtained. Anal. Calcd for $C_{16}H_{36}NReS_4$: C, 34.51; H, 6.52; N, 2.52; Re, 33.43; S, 23.03. Found: C, 34.43; H, 6.27; N, 2.53; Re, 33.51; S, 23.24. Absorption spectrum (acetonitrile): λ_{max} 580 (ϵ_M 440), 509 (12 700), 347 (2070), 311 (24 300), 264 (sh, 3090) nm. IR spectrum (KBr): 484 cm^{-1} (ν_{ReS}). ^{187}Re NMR spectrum (acetonitrile): 2586 ppm ($\Delta_{1/2} \simeq$ 1100 Hz, downfield of (n-Bu_4N)[ReO_4]).

(Et$_4$N)$_3$[VFe$_2$S$_4$Cl$_4$]. To a stirred solution of 6.85 g (15 mmol) of $(Et_4N)_2[FeCl_4]$ in ~150 mL of acetonitrile was added 1.75 g (7.5 mmol) of $(NH_4)_3[VS_4]$. The color of the slurry changed immediately to deep wine red. After the solution was stirred for ~30 min, some black solid was removed. Enough ether was added to the filtrate until some dark oily droplets started to separate. After ~10 min of standing, the mixture was filtered and ether was added to the filtrate until incipient crystallization. The contents were left standing overnight at −20 °C. The crude product was collected, washed with ether, and dried in vacuo. Recrystallization from acetonitrile/ether afforded 2.8 g (45%) of pure product as a black-red solid. Anal. Calcd for $C_{24}H_{60}Cl_4Fe_2N_3S_4V$: C, 34.99; H, 7.36; Cl, 17.22; Fe, 13.56; N, 5.35; S, 15.57; V, 6.18. Found: C, 34.67; H, 7.28; Cl, 17.63; Fe, 13.50; N, 5.35; S, 15.67; V, 6.43. Absorption spectrum (acetonitrile): λ_{max} 232 (ϵ_M 32 100), 250 (sh), 310 (13 600), 350 (sh), 396 (5500), 516 (6400), 700 (sh) nm. IR spectrum (KBr): 470, 462 (sh) (ν_{VS}) cm^{-1}.

(Me$_4$N)$_3$[VFe$_2$S$_4$Cl$_4$]·DMF. To a slurry of 1.89 g (5.5 mmol) of $(Me_4N)_2[FeCl_4]$ in ~50 mL of acetonitrile was added 0.64 g (2.8 mmol) of $(NH_4)_3[VS_4]$. An immediate color change ensued, resulting in a wine red solution that was stirred overnight at room temperature. The purple-red solid thus formed was collected, washed with acetonitrile, and dried in vacuo. Recrystallization from DMF/ether afforded 1.04 g (58%) of dark black-red crystalline product. The composition and crystal structure of this compound were established by single-crystal X-ray analysis.

(Et$_4$N)$_3$[VFe$_2$S$_4$(SPh)$_4$]. (a) From (Et$_4$N)$_2$[Fe$_4$(SPh)$_{10}$]. To a stirred solution of 1.69 g (1.07 mmol) of $(Et_4N)_2[Fe_4(SPh)_{10}]$ and 0.71 g (4.3 mmol) of Et_4NCl in 50 mL of acetonitrile was added 0.50 g (2.2 mmol) of $(NH_4)_3[VS_4]$. The color of the solution changed from golden brown to dark red. After being stirred for 1 h at room temperature, the contents were filtered to remove a purple-black solid. The concentrated filtrate from solvent removal was treated with ether until cloudiness was evident. Storage at −20 °C afforded a crystalline product, which was collected and recrystallized from acetonitrile. Black-red crystals were collected, washed with ether, and dried in vacuo, affording 1.0 g (42%) of pure product. Anal. Calcd for $C_{48}H_{80}Fe_2N_3S_8V$: C, 51.55; H, 7.21; Fe, 9.99; N, 3.76; S, 22.94; V, 4.56. Found: C, 50.78; H, 7.14; Fe, 9.94; N, 3.82; S, 22.55; V, 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) nm. ^{1}H NMR spectrum (CD_3CN, 303 K): 32.7 (m-H), −23.4 (o-H); −29.9 (p-H) ppm. IR spectrum (KBr): 476, 461 (ν_{VS}) cm^{-1}.

(b) From (Et$_4$N)$_2$[Fe(SPh)$_4$]. A stirred gray-brown solution of 3.2 g (4.2 mmol) of $(Et_4N)_2[Fe(SPh)_4]$ in ~50 mL of acetonitrile was treated with 0.50 g (2.1 mmol) of $(NH_4)_3[VS_4]$. The resulting wine red solution was stirred for 1 h at ambient temperature, after which the contents were filtered. Addition of ether to the concentrated filtrate from solvent removal in vacuo, and cooling at −20 °C, caused separation of a black-red crystalline solid. This material was collected, washed with ether, and dried in vacuo to give 1.1 g (46%) of product. The ^{1}H NMR spectrum of this product is identical with that of the compound prepared by method a.

(Me$_4$N)$_3$[VFe$_2$S$_4$(SPh)$_4$]. To a stirred greenish yellow solution of 2.0 g (1.4 mmol) of $(Me_4N)_2[Fe_4(SPh)_{10}]$ and 0.60 g (5.5 mmol) of Me_4NCl in ~150 mL of acetonitrile was added 0.64 g (2.7 mmol) of $(NH_4)_3[VS_4]$. The solution changed slowly to brownish red and then to dark red after being stirred for ~24 h at room temperature. The contents were filtered, and the volume of the filtrate was reduced in vacuo at 50 °C until a purple-red crystalline solid began to separate. Solid formed upon cooling of the mixture at −20 °C was collected, washed with ether, and dried in vacuo. Addition of ether to the filtrate afforded a second crop of solid. The combined yield was 1.5 g (66%) of product as needle-shaped, purple-red crystals. The ^{1}H NMR spectrum of this product revealed the same phenyl ring proton chemical shifts as those of the Et_4N^+ salt.

(n-Bu$_4$N)$_3$[VS$_4$(CuCN)$_3$]·2CH$_3$COCH$_3$. Addition of 1.2 g (5.1 mmol) of $(NH_4)_3[VS_4]$ to a slurry of 0.46 g (5.1 mmol) of CuCN and 0.25 g (5.1 mmol) of NaCN in 70 mL of H_2O caused an immediate color change to bright wine red. After the contents were stirred for 4 h at room temperature, black solid was removed by filtration. To the filtrate was added a solution of 6.6 g (21 mmol) of n-Bu_4NBr in a minimum volume of H_2O, causing separation of a red crystalline material, which was collected, washed well with H_2O, 9:1 v/v ether/ethanol, and ether, and dried in vacuo. The crude product was dissolved in a minimum volume of acetone, and ether was added to incipient crystallization. Cooling at −20 °C afforded a crystalline solid, which was collected, washed with ether, and dried in vacuo; 1.3 g (59% based on Cu) of analytically pure compound was obtained as red crystals. Anal. Calcd for $C_{57}H_{120}Cu_3N_6O_2S_4V$: C, 53.01; H, 9.37; Cu, 14.76; N, 6.51; S, 9.93; V, 3.95. Found: C, 52.27; H, 9.31; Cu, 15.17, N, 6.38; S, 10.41; V, 3.98. Absorption spectrum (acetonitrile): λ_{max} 260 (relative intensity 1), 336 (sh, 0.83), 354 (0.91), 400 (sh, 0.38), 524 (0.18) nm. IR spectrum (KBr): 2109 (ν_{CN}); 489, 473, 458 (ν_{VS}) cm^{-1}.

Collection and Reduction of X-ray Data. Suitable crystals of compounds listed in Table I were obtained as follows: black-purple $(NH_4)_3[VS_4]$, slow cooling of the filtrate prepared as described above; black (n-Bu_4N)[ReS_4], slow cooling of an acetonitrile/ether solution; black-red $(Me_4N)_3[VFe_2S_4Cl_4]$·DMF, slow vapor diffusion of ether into a DMF solution. Crystals were mounted in glass capillaries and sealed under argon or dinitrogen. Diffraction studies were performed at ambient temperature on a Nicolet R3m four-circle automated diffractometer with a Mo X-ray source equipped with a graphite monochromator. The final orientation matrix and unit cell parameters were determined by least-squares treatment of 25 machine-centered reflections having 25° ≤ 2θ ≤ 30° (for $(NH_4)_3[VS_4]$) and 20° ≤ 2θ ≤ 25° (for the other compounds). The intensities of three check reflections were measured every 123 reflections during data acquisition and revealed no significant changes in intensities. The crystal parameters and details of the data collection are summarized in Table I. The SHELXTL programs (Nicolet XRD Corp., Madison, WI) XTAPE and XEMP were used for data processing and empirical absorption corrections, respectively. Corrections were applied to all data sets.

Structure Solution and Refinement. The SHELXTL program package was used throughout. Heavy-atom positions were revealed by the direct-methods program SOLV. All remaining non-hydrogen atoms were located with use of successive difference Fourier maps and blocked-cascade least-squares refinement. Atomic scattering factors were taken from a standard source.[20] In the last stages of refinement of (n-Bu_4N)[ReS_4] and $(Me_4N)_3[VFe_2S_4Cl_4]$·DMF, fixed contributions were included from hydrogen atoms with a C–H distance of 0.96 Å and isotropic thermal parameters 1.2× that of the bonded carbon atom. With $(NH_4)_3[VS_4]$ all hydrogen atoms were located from difference Fourier maps and were refined. Final R factors and other data are included in Table I. Individual structural refinements are briefly described.

(a) (NH$_4$)$_3$[VS$_4$]. The systematic absences $0kl$ ($k + l = 2n + 1$) and $hk0$ ($h = 2n + 1$) uniquely define the space group *Pnma* (No. 62). The asymmetric unit consists of $^1/_2$ anion and $1^1/_2$ cations, the remainder being generated by a plane of symmetry. With use of 1423 unique data, convergence was reached at R = 10.3% for isotropic, and at R = 3.3% for anisotropic, refinement of all non-hydrogen atoms. At this stage all hydrogen atoms were included and isotropically refined. A final difference Fourier map revealed one peak (0.46 e/Å^3) near the V atom and

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Table I. Summary of Crystal Data, Intensity Collections, and Structure Refinement Parameters for $(NH_4)_3[VS_4]$, $(n\text{-}Bu_4N)[ReS_4]$, and $(Me_4N)_3[VFe_2S_4Cl_4]\cdot DMF$

	$(NH_4)_3[VS_4]$	$(n\text{-}Bu_4N)[ReS_4]$	$(Me_4N)_3[VFe_2S_4Cl_4]\cdot DMF$
formula	$H_{12}N_3S_4V$	$C_{16}H_{36}NReS_4$	$C_{15}H_{43}Cl_4Fe_2N_4OS_4V$
mol wt	233.31	556.93	728.24
a, Å	9.432 (2)	11.355 (2)	16.058 (3)
b, Å	10.825 (2)	11.334 (2)	11.371 (2)
c, Å	9.309 (2)	18.566 (2)	19.856 (4)
β, deg			110.20 (1)
V, Å^3	950.2 (3)	2389.4 (8)	3403 (1)
cryst syst	orthorhombic	orthorhombic	monoclinic
Z	4	4	4
d_{calcd} (d_{obsd}), g/cm^3	1.63 (1.65)^a	1.55 (c)	1.42 (1.42)^b
space group	*Pnma*	*Pcnn*	$P2_1/c$
cryst dimens, mm	0.38 × 0.44 × 0.46	0.30 × 0.34 × 0.78	0.28 × 0.35 × 0.46
radiation	Mo K$\bar{\alpha}$ (λ = 0.71069 Å)	Mo K$\bar{\alpha}$ (λ = 0.71069 Å)	Mo K$\bar{\alpha}$ (λ = 0.71069 Å)
abs coeff, μ, cm^{-1}	37.3	57.1	17.0
transmission factors (max/min)	0.216/0.183	0.116/0.082	0.616/0.549
scan speed, deg/min	2.0–29.3 ($\theta/2\theta$ scan)	2.0–29.3 ($\theta/2\theta$ scan)	2.0–29.3 ($\theta/2\theta$ scan)
2θ limits	$3° \leq 2\theta \leq 65°$	$3° \leq 2\theta \leq 52°$	$3° \leq 2\theta \leq 50°$
scan range, deg	$2.0 + (2\theta_{K\alpha_1} - 2\theta_{K\alpha_2})$	$1.3 + (2\theta_{K\alpha_1} - 2\theta_{K\alpha_2})$	$2.0 + (2\theta_{K\alpha_1} - 2\theta_{K\alpha_2})$
bkgd/scan time ratio	0.10	0.25	0.25
data collected	1804 ($+h,+k,+l$)	2363 ($+h,+k,+l$)	5868 ($\pm h,+k,+l$)
R_{merge},^{d} %	2.2	0.7	1.6
unique data ($I > 3\sigma(I)$)	1423	1222	3540
no. of variables	69	101	278
goodness of fit (GOF)^e	1.113	1.229	1.553
$R(R_w)$,^{f} %	2.60 (2.85)	4.14 (4.97)	5.04 (5.58)

^{a}Determined by the neutral buoyancy technique in CCl_4/CH_2Br_2. ^{b}CCl_4/n-hexane. ^{c}Not measured. ^{d}$R_{merge} = [\sum N_i \sum_{j=1}^{N_i} (\bar{F}_j - F_j)^2 / \sum (N_i - 1) \sum_{j=1}^{N_i} F_j^2]^{1/2}$, where N_i is the number of reflections in a given set, F_j is one member of the set, and $\bar{F}_j$ is the mean. ^{e}GOF $= [\sum w(|F_o| - |F_c|)^2 / (N_{observns} - N_{parameters})]^{1/2}$, $w = [\sigma^2(F) + gF^2]^{-1}$. ^{f}$R = [\sum ||F_o| - |F_c|| / \sum |F_o|]$, $R_w = [\sum w(|F_o|^2 - |F_c|^2) / \sum w|F_o|^2]^{1/2}$. g = 0.0005 for $(NH_4)_3[VS_4]$, 0.001 65 for $(n\text{-}Bu_4N)[ReS_4]$, and 0.009 for $(Me_4N)_3[VFe_2S_4Cl_4]\cdot DMF$.

several random features (≲0.43 e/Å^3).

(b) $(n\text{-}Bu_4N)[ReS_4]$. The systematic absences $hk0$ ($h + k = 2n + 1$), $h0l$ ($h + l = 2n + 1$), and $0kl$ ($l = 2n + 1$) uniquely define the space group *Pcnn* (nonstandard setting of *Pnna*, No. 52, equivalent positions $\pm(x, y, z; -x, y, {}^1/_2 + z; {}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z; {}^1/_2 - x, {}^1/_2 - y, z))$. This choice was confirmed by successful solution and refinement of the structure. The asymmetric unit consists of $^1/_2$ anion and $^1/_2$ cation, the remainder being generated by a twofold axis. Isotropic and anisotropic refinements of all non-hydrogen atoms converged at R = 12.1% and 5.4%, respectively. Hydrogen atoms were then included as above. A final difference Fourier map revealed several random features (≲0.85 e/Å^3) around the Re atom.

(c) $(Me_4N)_3[VFe_2S_4Cl_4]\cdot DMF$. The systematic absences $h0l$ ($h = 2n + 1$) and $0k0$ ($k = 2n + 1$) uniquely define the space group $P2_1/c$ (No. 14). With use of 3540 unique data convergence was reached at R = 12.5% for isotropic, and at R = 6.1% for anisotropic, refinement of all non-hydrogen atoms. The DMF solvate molecule is moderately disordered and was isotropically refined with fractional site occupancies: two molecules with site occupancy factors of 0.85 and 0.15. The C=O unit in the molecule with a site occupancy factor of 0.85 is disordered and appears at two sites with occupancy factors of 0.60 and 0.25. In the final refinement all hydrogen atoms except those of DMF were included. A final difference Fourier map revealed several random features (≲0.83 e/Å^3) near the DMF molecule.

Atom positional parameters for the three structures are listed in Table II.[21] Selected metric data for the three anions are presented in Tables III and IV. Cation dimensions are entirely standard and are not tabulated.

Other Physical Measurements. All measurements were made under anaerobic conditions. Electronic spectra were recorded on a Cary Model 219 spectrophotometer. NMR spectra were obtained with a Bruker WM-300 spectrometer equipped with a deuterium lock and operating at 300.13 (^1H) and 68.29 (^{187}Re) MHz for the indicated nuclei. Samples containing the latter nucleus were measured in 10 mm o.d. NMR tubes equipped with vortex plugs. Chemical shifts are reported vs. the external standards Me_4Si (^1H) and $(n\text{-}Bu_4N)[ReO_4]$ (^{187}Re) in CD_3CN solutions. Shifts downfield of the references are designated as positive. Infrared spectra were measured with a Perkin-Elmer 599B spectrophotometer and were referenced to the 1028-cm^{-1} band of a 0.05-mm polystyrene film. Solid-state magnetic susceptibilities were determined by the Faraday method. Solution magnetic susceptibilities were measured by the NMR technique with 5 mm o.d. coaxial tubes and Me_4Si internal standard. Diamagnetic corrections were taken from tabulated values.[22]

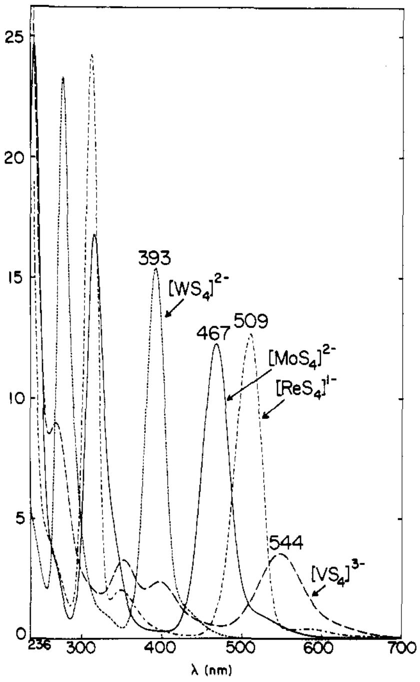

Figure 1. Absorption spectra of $(NH_4)_2[MS_4]$ (M = Mo, W) in aqueous solution, $(NH_4)_3[VS_4]$ in 1 M aqueous NaOH (freshly prepared solution), and $(n\text{-}Bu_4N)[ReS_4]$ in acetonitrile. For each ion λ_{max} of the lowest energy band is given.

Results and Discussion

$[VS_4]^{3-}$ and $[ReS_4]^-$. These ions were prepared by the reaction of H_2S with aqueous solutions of NH_4VO_3 and NH_4ReO_4. The preparations given are more detailed than those previously reported.[9,12a] $[ReS_4]^-$ is easily isolated as its $n\text{-}Bu_4N^+$ salt, which is freely soluble in polar organic solvents but sparingly soluble

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(21) See paragraph at the end of this article concerning supplementary material available.

(22) O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 203.

Table II. Atom Positional Parameters (×10^4)

atom	*x*	*y*	*z*
	$(NH_4)_3[VS_4]$		
V	2212 (1)[a]	2500	194 (1)
S(1)	2049 (1)	2500	2482 (1)
S(2)	86 (1)	2500	−712 (1)
S(3)	3311 (1)	4143 (1)	−480 (1)
N(1)	−3533 (3)	2500	−930 (3)
N(2)	−490 (2)	4606 (2)	2069 (2)
	(*n*-Bu_4N)[ReS_4]		
Re	2500	2500	5990 (1)
S(1)	1846 (3)	1115 (2)	6644 (2)
S(2)	3891 (4)	1794 (5)	5356 (3)
N	2500	2500	9394 (5)
C(11)	3272 (7)	1708 (7)	8933 (4)
C(12)	4112 (9)	2298 (7)	8421 (5)
C(13)	4797 (9)	1419 (10)	8006 (6)
C(14)	5668 (9)	1861 (12)	7480 (7)
C(21)	1724 (7)	1717 (8)	9855 (4)
C(22)	2319 (8)	993 (9)	10419 (6)
C(23)	1394 (10)	274 (11)	10833 (6)
C(24)	1863 (14)	−380 (15)	11410 (8)
	$(Me_4N)_3[VFe_2S_4Cl_4]\cdot DMF$		
V	2822 (1)	4892 (1)	5737 (1)
Fe(1)	2856 (1)	2857 (1)	6481 (1)
Fe(2)	2786 (1)	6742 (1)	4857 (1)
S(1)	2072 (1)	3295 (2)	5321 (1)
S(2)	1944 (1)	6411 (2)	5547 (1)
S(3)	3496 (1)	4624 (2)	6886 (1)
S(4)	3773 (1)	5224 (2)	5198 (1)
Cl(1)	1983 (1)	2188 (2)	7087 (1)
Cl(2)	1940 (2)	6725 (3)	3678 (1)
Cl(3)	3930 (1)	1479 (2)	6620 (1)
Cl(4)	3478 (1)	8511 (2)	5064 (1)
N(1)	3678 (3)	6610 (4)	2601 (3)
C(1)	4173 (5)	6757 (6)	2095 (4)
C(2)	4151 (5)	5756 (6)	3156 (4)
C(3)	3594 (5)	7751 (6)	2921 (5)
C(4)	2770 (5)	6149 (7)	2190 (4)
N(2)	3792 (4)	3224 (5)	−838 (3)
C(5)	4150 (6)	4250 (7)	−1111 (4)
C(6)	4194 (5)	3206 (7)	−40 (4)
C(7)	2820 (6)	3360 (10)	−1042 (5)
C(8)	4049 (7)	2157 (7)	−1137 (5)
N(3)	−204 (4)	4447 (5)	3236 (3)
C(9)	576 (7)	3966 (9)	3094 (7)
C(10)	−1037 (6)	3795 (10)	2925 (6)
C(11)	1 (6)	4662 (12)	4000 (5)
C(12)	−336 (8)	5678 (9)	2924 (8)
N(4)	882 (7)	5209 (7)	9597 (5)
O	46 (7)	3871 (10)	8692 (6)
C(13)	345 (10)	6277 (10)	9331 (10)
C(14)	1463 (8)	5280 (11)	10357 (5)
C(15)	634 (11)	4177 (10)	9260 (8)
O(1)	536 (12)	4257 (15)	8587 (10)
C(13a)	342 (13)	6285 (12)	9387 (16)
C(15a)	1119 (12)	4480 (15)	9170 (8)
N(4b)	251 (10)	5559 (14)	9193 (13)
O(2)	−518 (15)	3881 (12)	8623 (14)
C(13b)	1179 (11)	5158 (16)	9501 (16)
C(14b)	77 (16)	6667 (14)	9505 (14)
C(15b)	−447 (13)	4926 (13)	8802 (15)

[a] Estimated standard deviations in parentheses in this and succeeding tables.

in water. $[VS_4]^{3-}$ has been obtained in this and prior work only as its NH_4^+ salt, which is quite soluble in aqueous alkaline solution. We have thus far been unable to metathesize this compound to a pure R_4N^+ or Ph_4P^+ salt for use in nonaqueous solvents.

(a) Spectral Features. Absorption spectra of the four known transition element tetrathiometalates are compared in Figure 1. Solutions of $[VS_4]^{3-}$ and $[ReS_4]^-$ are deep red-violet and blue-violet, respectively. The spectra arise entirely from LMCT transitions and have been analyzed in tetrahedral symmetry.[11,12,13b] Another consequence of this symmetry is the observation of ^{185,187}Re NMR. While these nuclei have good receptivities, their large quadrupole moments coupled to significant electric field gradients produce rapid nuclear relaxation and attendant very large line widths that may prevent signal detection for compounds with less than cubic symmetry. The only previous Re NMR spectrum reported is that of aqueous $NaReO_4$.[23] Shown in Figure 2 are the ^{187}Re NMR spectra[24] of the *n*-Bu_4N^+ salts of $[ReO_4]^-$ and $[ReS_4]^-$ in CD_3CN solutions at ambient temperature. The spectra

Table III. Selected Interatomic Distances (Å) and Angles (deg) in the Anions of $(NH_4)_3[VS_4]$ and (*n*-Bu_4N)[ReS_4]

	$[VS_4]^{3-}$		
V–S(1)	2.135 (1)	V–S(3)	2.153 (1)
V–S(2)	2.175 (1)	mean (of 4)	2.154 (16)
S(1)–V–S(2)	108.7 (1)	S(3)–V–S(3′)	111.5 (1)
S(1)–V–S(3)	109.0 (1)	mean (of 6)	109.5 (10)
S(2)–V–S(3)	109.3 (1)		
	$[ReS_4]^-$		
Re–S(1)	2.118 (3)	mean	2.123 (5)
Re–S(2)	2.126 (5)		
S(1)–Re–S(2)	107.4 (2)	S(2)–Re–S(2a)	112.8 (3)
S(1)–Re–S(1a)	110.1 (2)	mean (of 6)	109.5 (20)
S(1)–Re–S(2a)	109.6 (2)		

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $(Me_4N)_3[VFe_2S_4Cl_4]\cdot DMF$

Fe(1)···Fe(2)	5.450 (2)	Fe(1)–S(1)	2.267 (2)
		Fe(1)–S(3)	2.273 (3)
V···Fe(1)	2.737 (2)	Fe(2)–S(2)	2.265 (3)
V···Fe(2)	2.723 (2)	Fe(2)–S(4)	2.283 (3)
mean	2.730 (10)	mean	2.272 (8)
V–S(1)	2.178 (2)	Fe(1)–Cl(1)	2.271 (3)
V–S(2)	2.178 (2)	Fe(1)–Cl(3)	2.276 (3)
V–S(3)	2.184 (2)	Fe(2)–Cl(2)	2.265 (3)
V–S(4)	2.179 (3)	Fe(2)–Cl(4)	2.266 (3)
mean	2.178 (5)	mean	2.270 (3)
Fe(1)–V–Fe(2)	172.9 (1)	S(1)–Fe(1)–S(3)	101.0 (1)
		S(2)–Fe(2)–S(4)	101.1 (1)
S(1)–V–S(3)	106.8 (1)		
S(2)–V–S(4)	107.4 (1)	Cl(1)–Fe(1)–Cl(3)	106.6 (1)
		Cl(2)–Fe(2)–Cl(4)	106.1 (1)
S(1)–V–S(2)	110.8 (1)		
S(1)–V–S(4)	110.4 (1)	S(1)–Fe(1)–Cl(1)	112.6 (1)
S(3)–V–S(2)	110.4 (1)	S(1)–Fe(1)–Cl(3)	113.9 (1)
S(3)–V–S(4)	111.0 (1)	S(3)–Fe(1)–Cl(1)	113.3 (1)
		S(3)–Fe(1)–Cl(1)	109.5 (1)
V–S(1)–Fe(1)	76.0 (1)	S(2)–Fe(2)–Cl(2)	110.7 (1)
V–S(3)–Fe(1)	75.7 (1)	S(2)–Fe(2)–Cl(4)	113.3 (1)
V–S(2)–Fe(2)	75.5 (1)	S(4)–Fe(2)–Cl(2)	114.1 (1)
V–S(4)–Fe(2)	75.2 (1)	S(4)–Fe(2)–Cl(4)	111.8 (1)

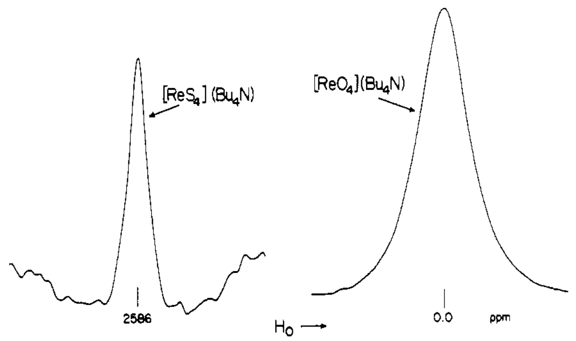

Figure 2. ^{187}Re NMR spectra of ~0.1 M (*n*-Bu_4N)[ReX_4] (X = O, S) in CD_3CN solution at ~297 K, recorded with the same magnetic field scale.

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(23) Dwek, R. A.; Luz, Z.; Shporer, M. *J. Phys. Chem.* **1970**, *74*, 2232.

(24) ^{187}Re: 62.93% natural abundance, receptivity/^{13}C 4900, $I = {}^5/_2$, Q = 2.6.

are readily observed and have line widths of 3030 and 1100 Hz, respectively. The chemical shift difference of 2586 ppm, with $[ReS_4]^-$ being the less shielded, is close to $[MoO_4]^{2-}/[MoS_4]^{2-}$ values of 2209[2] and 2258[25] ppm in acetonitrile and aqueous solutions, respectively. The corresponding difference for tungsten anions in aqueous solution is 3769 ppm.[25]

(b) Structures. The structures of $[VS_4]^{3-}$ and $[ReS_4]^-$, as the NH_4^+ and n-Bu_4N^+ salts, respectively, are shown in Figure 3, and dimensional data are collected in Table III. An early, very brief report of the crystal structure of $(NH_4)_3[VS_4]$ established orthorhombic space group *Pnma* and unexpectedly different V–S distances of one each at 2.09 and 2.16 Å and two at 2.18 Å.[14] Our redetermination of the structure yielded all cell parameters within 0.04 Å of those previously reported. The crystal contains well-separated cations and anions, with a mean N–H distance in the former of 0.85 (12) Å. One of the NH_4^+ ions and the $[VS_4]^{3-}$ ion have crystallographically imposed C_s symmetry. The latter exhibits slightly distorted T_d symmetry, but with the range of V–S bond distances (2.135 (1)–2.175 (1) Å) being substantially smaller than that found earlier.[14] The compound $(Ph_4P)[ReS_4]$ was found to be isostructural with tetragonal $(Ph_4P)[FeCl_4]$, and the mean Re–S distance of 2.155 (30) Å was evaluated by a powder radial distribution analysis.[15] The present single-crystal determination of $(n\text{-}Bu_4N)[ReS_4]$ reveals discrete cations and anions with imposed C_2 symmetry. The $[ReS_4]^-$ ion displays a somewhat distorted tetrahedral structure. The dihedral angle between planes S(1)ReS(1a) and S(2)ReS(2a) is 88.4°. The mean Re–S bond distance of 2.123 (5) Å is more accurate than the previous value and is indistinguishable from the distance of 2.125 (6) Å in $Rb[ReO_3S]$.[26] Accurate structures are now available for all transition-element $[MS_4]^{z-}$ ions.[27,28] The order of mean bond lengths is Re–S < V–S < Mo–S ≃ W–S, the first two being in the reverse order predicted from tetrahedral Shannon radii.[29] Despite its third-row position, Re with its higher formal charge apparently overrides intrinsic relative sizes when bound to a highly polarizable ligand.

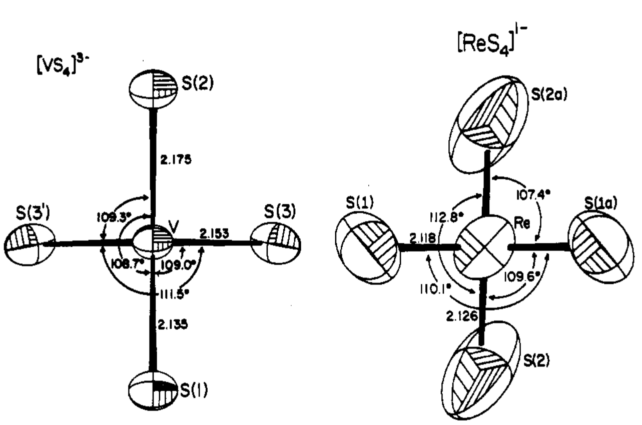


Figure 3. Structures of $[VS_4]^{3-}$ and $[ReS_4]^-$, showing 50% probability ellipsoids, atom-labeling schemes, and selected bond distances and angles.

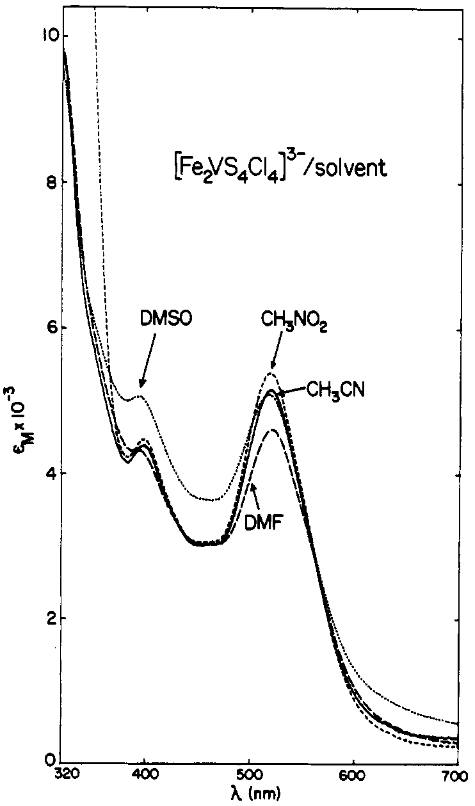


Figure 4. Absorption spectra of ~2 mM $[VFe_2S_4Cl_4]^{3-}$ in solvents of different coordinating tendencies.

(c) Reactions with Fe(II). The ions $[MS_4]^{2-}$ (M = Mo, W) are precursors to a large variety of linear clusters,[5-7] including those containing Fe(II). Homogeneous reactions 1–4 in aprotic

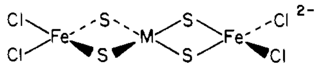
$$FeCl_2 + [MS_4]^{2-} \rightarrow [Cl_2FeS_2MS_2]^{2-} \quad (1)$$

$$[Cl_2FeMS_4]^{2-} + FeCl_2 \rightleftharpoons [MFe_2S_2Cl_4]^{2-} \quad (2)$$

$$[MFe_2S_4Cl_4]^{2-} + MS_4^{2-} \rightarrow 2[Cl_2FeS_2MS_2]^{2-} \quad (3)$$

$$[(PhS)_2FeMS_4]^{2-} + 2FeCl_3 \rightarrow [MFe_2S_4Cl_4]^{2-} + PhSSPh + FeCl_2 \quad (4)$$

1



2

media lead to the bi- and trinuclear species **1**[30,31] (L = Cl⁻) and **2**,[32,33] respectively. Similar reaction systems have been investigated with $[VS_4]^{3-}$ and $[ReS_4]^-$. Inasmuch as the former is available only as its NH_4^+ salt, somewhat soluble in DMF (with, however, a color change to blue-violet) and insoluble in acetonitrile, reaction 5 proceeds in the presence of a soluble excess of the Fe(II)

$$(NH_4)_3[VS_4] + 2(R_4N)_2[FeCl_4] \xrightarrow{MeCN} (R_3N)_3[VFe_2S_4Cl_4] + R_4NCl + 3NH_4Cl \quad (5)$$

reactant. As a consequence, reactions with a 1:1 or 1:2 V:Fe stoichiometry yield only the trinuclear cluster. The compounds $(Me_4N)_3[VFe_2S_4Cl_4]\cdot DMF$ (58%) and $(Et_4N)_3[VFe_2S_4Cl_4]$ (45%) were isolated as black-red crystals in the indicated purified yields from reactions with a 1:2 stoichiometry. No reaction was observed

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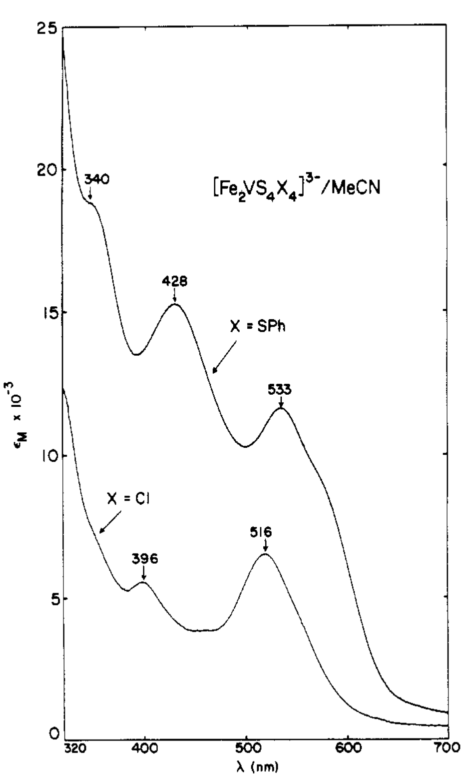

Figure 5. Absorption spectra of $[VFe_2S_4X_4]^{3-}$ ($X = Cl^-, PhS^-$) in acetonitrile solution.

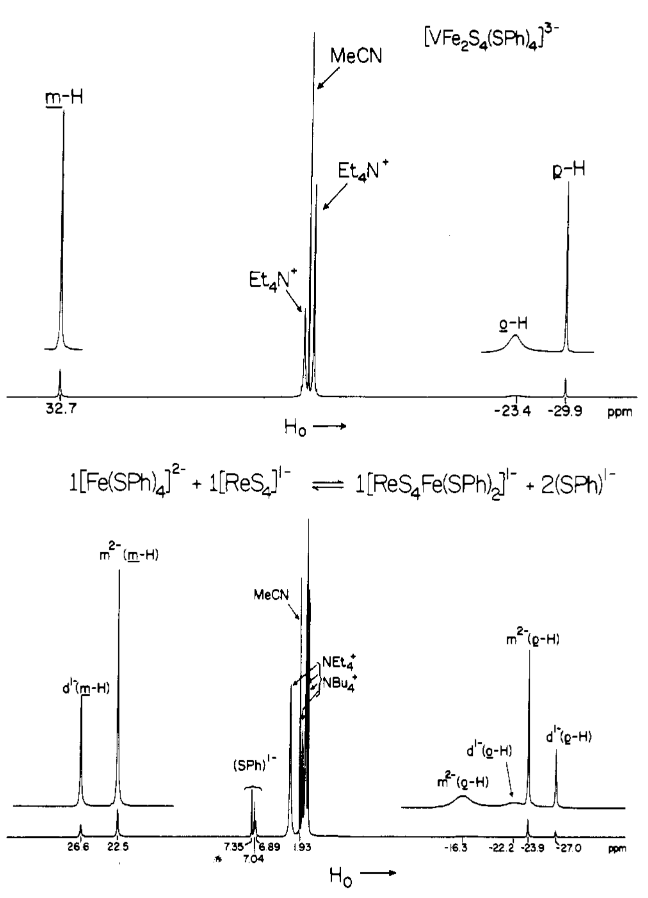

Figure 6. ^1H NMR spectra in CD_3CN solutions: (upper) $(Et_4N)_3[VFe_2S_4Cl_4]$ at 303 K; (lower) solution initially containing equimolar (~40 mM) $(Et_4N)_2[Fe(SPh)_4]$ (m^{2-}) and (n-Bu_4N)$[ReS_4]$ at ~297 K, showing formation of $[(PhS)_2FeReS_4]^-$ (d^{1-}). Signal assignments are indicated.

between $[VFe_2S_4Cl_4]^{3-}$ and excess $(NH_4)_3[VS_4]$ in acetonitrile. Electronic spectra of $[VFe_2S_4Cl_4]^{3-}$ (λ_{max} 396, 516 nm) in Figure 4 reveal significant perturbation of the $[VS_4]^{3-}$ chromophore and a near-constancy in solvents of widely different coordinating ability. These results indicate the absence of dissociative equilibrium 6;

$$[VFe_2S_4Cl_4]^{3-} \rightleftharpoons [Cl_2FeS_2VS_2]^{3-} + FeCl_2 \qquad (6)$$

consequently, no reaction occurs with excess $(NH_4)_3[VS_4]$. In comparison, reactions 2 and 3 have been reported for M = Mo and W.[32a] By virtue of its higher negative charge, $[VS_4]^{3-}$ has an enhanced affinity for bridging two $FeCl_2$ groups compared to $[MS_4]^{2-}$ as a bridge. At present, $[Cl_2FeVS_4]^{3-}$, whose analogues **1** are stable, must be considered an unknown species.

The benzenethiolate cluster $[VFe_2S_4(SPh)_4]^{3-}$ was prepared in good purified yields as its Et_4N^+ and Me_4N^+ salts from two Fe(II) sources by reactions 7 and 8. The following observations indicate

$$2[Fe(SPh)_4]^{2-} + [VS_4]^{3-} \xrightarrow{MeCN} [VFe_2S_4(SPh)_4]^{3-} + 4PhS^- \qquad (7)$$

$$[Fe_4(SPh)_{10}]^{2-} + 2[VS_4]^{3-} \xrightarrow{MeCN} 2[VFe_2S_4(SPh)_4]^{3-} + 2PhS^- \qquad (8)$$

that this cluster has a structure analogous to that of $[VFe_2S_4Cl_4]^{3-}$ (vide infra). (i) The absorption spectra in Figure 5 reveal rather similarly perturbed $[VS_4]^{3-}$ chromophores. (ii) Treatment of $[VFe_2S_4Cl_4]^{3-}$ with excess $(Et_4N)(SPh)$ in acetonitrile solution affords a species whose electronic and ^1H NMR spectra are identical with those of the product of reactions 7 and 8. The latter contains the same contact-shifted resonance pattern as found for $[(PhS)_2FeMS_4]^{2-}$.[31,34,35] The absence of any other signals demonstrates that ligand substitution reaction 9 proceeds cleanly, a

$$[VFe_2S_4Cl_4]^{3-} + 4PhS^- \xrightarrow{MeCN} [VFe_2S_4(SPh)_4]^{3-} + 4Cl^- \qquad (9)$$

process entirely similar to the formation of $[(RS)_2FeMoS_4]^{2-}$ from **1** ($L = Cl^-$).[31] (iv) The two bridging ν_{VS}-type vibrations at 476 and 461 cm^{-1} match closely those of $[VFe_2S_4Cl_4]^{3-}$ (470, 462 (sh) cm^{-1}), and as well those of **2** with M = Mo (470, 460 (sh) cm^{-1}) and W (468, 458 cm^{-1}).[32] (iv) The magnetic moment of 7.04 μ_B in the solid state at 300 K is essentially the same as that of solid $(Et_4N)_3[VFe_2S_4Cl_4]$ (7.01 μ_B). These values indicate two noninteracting high-spin Fe(II) atoms.

The complexing tendency of $[ReS_4]^-$ was examined in a reaction system containing equimolar (~40 mM) $[Fe(SPh)_4]^{2-}$ and $[ReS_4]^-$ in acetonitrile. The ^1H NMR spectrum of the system, shown in Figure 6, contains signals from unreacted $[Fe(SPh)_4]^{2-}$,[18] free PhS^-, and a new paramagnetic complex that exhibits contact-shifted phenyl proton signals. From relative signal intensities this species is identified as $[(PhS)_2FeReS_4]^-$, which is present in a ~1:1 mol ratio with $[Fe(SPh)_4]^{2-}$ in the equilibrium reaction of Figure 6. When examined by ^1H NMR in the same concentration range, $[VFe_2S_4(SPh)_4]^{3-}$ in the presence of excess $(Et_4N)(SPh)$ in acetonitrile did not detectably dissociate. Equivalent observations have been made for $[(PhS)_2FeMS_4]^{2-}$. The relatively smaller binding ability of $[ReS_4]^-$ follows from its lower charge, required by Re(VII), whose tendency to form short bonds, and thereby decrease the basicity of sulfido ligands, has been noted earlier. The influence of oxidation state and species charge on the chemical behavior of these elements is commonplace. Related examples in aqueous chemistry are the strong acid property of $HReO_4$ and the instability of $[MoO_4]^{2-}$, $[WO_4]^{2-}$, and especially $[VO_4]^{3-}$ to elimination of water and condensation except in alkaline solutions.[36]

Structure of $(Me_4N)_3[VFe_2S_4Cl_4]\cdot DMF$. The crystal structure of this compound consists of discrete cations, anions, and solvate molecules. The cations are unexceptional and are not further

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[35] For example, the M = Mo complex in CD_3CN solution at 298 K exhibits signals at +37.5 (m-H) and −37.8 (p-H) ppm.[34]

[36] Baes, C. F., Jr.; Mesmer, R. E. "The Hydrolysis of Cations"; Wiley: New York, 1976; pp 197–210, 253–260.

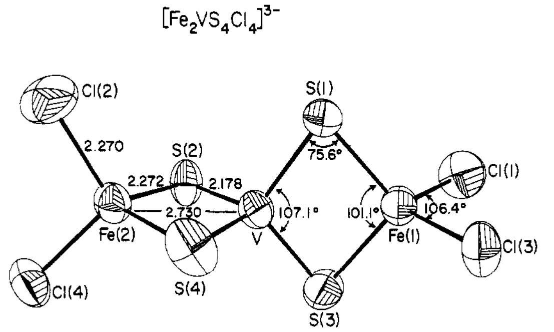


Figure 7. Structure of $[VFe_2S_4Cl_4]^{3-}$ as its Me_4N^+ salt/DMF solvate, showing 50% probability ellipsoids, atom-labeling scheme, and mean values of selected interatomic distances and angles.

Table V. Dihedral Angles (deg) between and Atom Position Deviations (Å) from Selected Unweighted Least-Squares Planes of $[VFe_2S_4Cl_4]^{3-}$

plane	deviation (±)	angle	
1. Fe(1)Cl(1)Cl(3)	0	1/2	92.1
2. Fe(1)S(1)S(3)V	0.053	1/3	5.1
3. Fe(2)S(2)S(4)V	0.062	1/4	94.6
4. Fe(2)Cl(2)Cl(4)	0	2/3	89.2
		2/4	4.7
		3/4	91.9

considered; solvate molecules are somewhat disordered. The structure of $[VFe_2S_4Cl_4]^{3-}$ is displayed in Figure 7, and selected interatomic distances and angles are listed in Table IV. Dihedral angles between and atom positional deviations from least-squares planes are contained in Table V.

The anion is composed of an array of three edge-shared tetrahedra with idealized overall D_{2d} symmetry. The $Fe(\mu\text{-}S)_2V(\mu\text{-}S)_2Fe$ core, a new structural unit, approaches linearity with Fe(1)–V–Fe(2) = 172.9 (1)°. The two $VFeS_2$ rhombs are not quite planar but are essentially perpendicularly disposed to each other. The central VS_4 subunit is a slightly distorted tetrahedron. Angles S(1)–V–S(3) and S(2)–V–S(4) are reduced below free ion values as a consequence of chelate ring formation. The remaining four angles are closer to those in $[VS_4]^{3-}$. Larger bond angle ranges are found for the S_2FeCl_2 fragments.

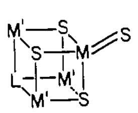
The mean V–S distance of 2.178 (5) Å shows an apparent elongation of 0.024 Å compared to free $[VS_4]^{3-}$ as a result of binding two $FeCl_2$ groups. Similar M–S increases occur with the M = Mo (0.027 Å) and W (0.044 Å) clusters **2** relative to free ion structures.[27a,28] These and other dimensions, averaged under D_{2d} symmetry, are compared in Table VI with corresponding mean values of $[MFe_2S_4Cl_4]^{2-}$ (**2**), whose cores are essentially linear. The mean Fe–S distance of 2.272 (8) Å in $[VFe_2S_4Cl_4]^{3-}$ is the shortest of this type. It reflects the higher negative charge of $[VS_4]^{3-}$ and the consequent stronger binding of $FeCl_2$ groups. The mean Fe–Cl distance of 2.270 (3) Å is much longer than that in various salts of $[FeCl_4]^-$[37] (2.18–2.19 Å) and is marginally longer than that in $[Fe_2S_2Cl_4]^{2-}$[38] (2.252 (8) Å), the only other example of a $Cl_2Fe(\mu\text{-}S)_2$ group, but one containing Fe(III). The mean Fe–Cl distance in the most accurate $[FeCl_4]^{2-}$ structure is 2.292 (2) Å.[39] The significantly shorter Fe–Cl bonds (by 0.04 Å in the Mo and W clusters is very probably a consequence of the M(VI) vs. V(V) oxidation state. The former apparently effects a differentially larger charge transfer from the Fe atom, thereby decreasing its Fe(II) character. Compared to data for $[FeCl_4]^{2-}$ and $[Fe(SPh)_4]^{2-}$, ^{57}Fe isomer shifts of $[MFe_2S_4Cl_4]^{2-}$ are smaller than expected[32,34,40] and are reflective of diminished d-orbital population. All of these results justify description of $[MS_4]^{2-}$ ions as charge-delocalizing ligands.[5,32,41]

Table VI. Comparative Structural Data[a] for $[MFe_2S_4Cl_4]^{2-,3-}$

	M = V[b]	M = Mo[c]	M = W[c]
Fe(1)···Fe(2)	5.450 (2)	5.552 (2)	5.603 (1)
M···Fe	2.730 (10)	2.775 (6)	2.802 (9)
M–S	2.178 (5)	2.204 (5)	2.209 (5)
Fe–S	2.272 (8)	2.295 (5)	2.320 (6)
Fe–Cl	2.270 (3)	2.225 (10)	2.233 (14)
Fe–M–Fe	172.9 (1)	179.4 (1)	179.3 (1)
M–S–Fe	75.6 (3)	76.1 (1)	76.4 (2)
Cl–Fe–Cl	106.4 (4)	110.2 (14)	111.2 (17)
S–Fe–S	101.1 (1)	101.0 (1)	100.0 (1)
S–V–S[d]	107.1 (4)	106.8 (3)	107.1 (1)
S–V–S[e]	110.7 (3)	110.8 (7)	110.6 (5)
S–Fe–Cl	112.4 (16)	111.4 (34)	111.3 (34)

[a] Distances (Å) and angles (deg) averaged under idealized D_{2d} symmetry; standard deviations from the mean (where applicable) are in parentheses. [b] This work. [c] Reference 32. [d] S atoms in same $MFeS_2$ unit. [e] S atoms in different $MFeS_2$ units.

In connection with the possible relevance to the problem of biological antagonism between copper and molybdenum, a number of complexes of $[MO_{4-n}S_n]^{2-}$ (M = Mo, W; n = 3, 4) with Cu(I) have been prepared[42-46] and reviewed.[47] Related reactions have been investigated with $[VS_4]^{3-}$. An aqueous reaction system containing equimolar amounts of $(NH_4)_3[VS_4]$, CuCN, and NaCN afforded the tetranuclear complex $[VS_4Cu_3(CN)_3]^{3-}$ as red crystals in the form of its $n\text{-}Bu_4N^+$ salt, acetone disolvate. Complexes with a 3:1 Cu:M ratio have been prepared, although not from CuCN. These are of three structural types, **3**–**5**[43-46] (M′ = Cu). Of these, **3** is known only with L = Cl^- and **4** has not been found with a terminal sulfide ligand. Type **5**, which applied to $[MS_4Cu_3Cl_3]^{2-}$,[43,44] is considered the most probable structure of $[VS_4Cu_3(CN)_3]^{3-}$. Thus far we have been unable to solve the crystal structure of $(n\text{-}Bu_4N)_3[VS_4Cu_3(CN)_3]\cdot 2Me_2CO$.[48]



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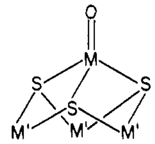

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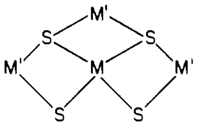

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Summary. The set $[MS_4]^{3-,2-,-}$ (M = V(V), Mo(VI), W(VI), Re(VII)) provides a particularly clear example wherein structural and reactivity properties are largely controlled by oxidation state

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and ion charge. The most significant are in the order of binding affinity $[ReS_4]^- < [MoS_4]^{2-} \simeq [WS_4]^{2-} < [VS_4]^{3-}$ toward $FeCl_2$, the ability of $[VS_4]^{3-}$ to form $[VFe_2S_4L_4]^{3-}$ with either hard ($L = Cl^-$) or soft ($L = PhS^-$) ligands, and the order of Fe–Cl distances $M = V > Mo \simeq W$, which is one measure of charge delocalization in $[MFe_2S_4Cl_4]^{3-,2-}$. The scope of the metal complex chemistry of $[VS_4]^{3-}$ remains to be defined. This point has been partly examined by means of reaction systems containing $(NH_4)_3[VS_4]$ and $(Et_4N)_2[ML_4]$ (M = Mn(II), Co(II), Ni(II), Cu(II) ($L = Cl^-$); Zn(II), Cd(II) ($L = Cl^-$, PhS^-)) in DMF or acetonitrile. Solution color changes were observed, followed by separation of amorphous black solids and decolorization of the solutions. The reaction between $[VS_4]^{3-}$ and AgCN gives a similar result. Evidently in these systems $[VS_4]^{3-}$ acts as a sulfide donor. However, the reaction system containing the mole ratio 3:1 $FeCl_2$:$(NH_4)_3[VS_4]$ in DMF affords in good yield the new cluster core $[VFe_3S_4]^{2+}$, with a cubane-type structure.[49] Clusters of this type will be the subject of our next report on V–Fe–S chemistry.

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Supplementary Material Available: X-ray structural data for $(NH_4)_3[VS_4]$, $(n\text{-}Bu_4N)[ReS_4]$, and $(Me_4N)_3[VFe_2S_4Cl_4]\cdot DMF$: anisotropic temperature factors, hydrogen atom coordinates and temperature factors, interatomic distances and angles in the cations, and calculated and observed structure factors (44 pages). Ordering information is given on any current masthead page.

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Contribution from the Laboratoire de Chimie Moléculaire, Unité Associée au CNRS, Université de Nice, Parc Valrose, 06034 Nice, France, and Laboratoire de Chimie Organique Physique, LA 321, Département de Recherches Fondamentales, Centre d'Etudes Nucléaires 85X, Université Scientifique et Médicale, 38041 Grenoble, France

Dibasic Character of a Bicyclic Aminophosphane. Formation and Crystal Structure of $H_3B\cdot\overline{P(OCMe_2CH_2)_2N}\cdot BH_3$

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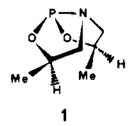
Phosphorus-bound borane adducts form first when diborane is allowed to react with the bicyclic aminophosphanes **1**–**3**. Then, notably, a second borane group is coordinated to the nitrogen site unless it is sterically hindered. All the compounds formed were isolated in good yields. The bis(borane) adducts are unusually stable. $H_3B\cdot\overline{P(OCMe_2CH_2)_2N}\cdot BH_3$ crystallizes in the monoclinic systems $P2_1/n$ with unit cell dimensions $a = 7.803$ (1) Å, $b = 16.650$ (1) Å, $c = 10.431$ (1) Å, $\beta = 95.1$ (1)°, and $Z = 4$. The dibasic character of ligand **2** is established by the existence of a B–P bond (1.873 (7) Å) and of a B–N bond (1.655 (8) Å). The P–N bond length (1.757 (4) Å) indicates the absence of π-bonding. The almost identical five-membered rings display a N-flap envelope conformation and are assembled in a helicoidal exo–endo arrangement (B–N–P–B dihedral angle 21.7°). NMR data (^{11}B and ^{31}P) establish that the B–P and B–N coordination bonds on **2b** and related bis(borane) adducts are preserved in solution. The basicity of the nitrogen atom of these cyclic aminophosphanes is further illustrated by the formation of the N-bonded BF_3 adduct $\overline{P(OCHMeCH_2)_2N}\cdot BF_3$ (**1c**).

Introduction

Although the description of the P–N bond and the extent of P_π–d_π interaction between the two atoms remains a subject of controversy,[1] it is a well-established experimental fact that aminophosphanes generally behave as P-donors only.[2] Restoration of the basicity of a tricoordinated nitrogen atom directly bonded to a phosphorus center appears to require constrained structures capable of forcing the nitrogen to retain its pyramidal geometry.[3,4] However, this nonplanarity is not in itself sufficient to induce coordination of the P-bound nitrogen to Lewis acids such as BH_3 or BF_3.[3] Finally, a few P- and N-bonded bis(borane) adducts have been obtained, and these were generally reported to be unstable.[3,5] The harder BF_3 is more inclined to coordinate at nitrogen, and N-bonded BF_3 adducts have indeed been reported to form with F_2PNMe_2[6] and $\overline{FPN(Me)(CH_2)_2NMe}$.[7] The recent obtainment of a stable adduct in which two borane groups are coordinated to two nitrogen atoms occupying apical positions on a five-coordinated bipyramidal phosphorus atom must also be mentioned.[8]

The bicyclic aminophosphanes **1**–**3**[9] are attractive because their bicyclic structure forces the P-bonded nitrogen atom to remain pyramidal; **1** is obtained as a mixture of meso and racemic diastereiosomers in 80:20 ratio and **3** as a pair of enantiomers.



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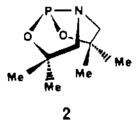

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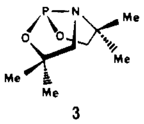

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The basicity of the nitrogen site in the bicyclic aminophosphanes **1** and **2** has now been confirmed by the formation of unusually

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[‡] Université Scientifique et Médicale de Grenoble.

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