and the resulting hydroxy acid was converted to the dimethyl ester 20 by sequential methylation (CH₂N₂), PDC oxidation, and a second methylation (CH₂N₂) (76% overall yield). The acetate was then removed from 21 (95%) and the carboxylic acid 21 was obtained by PDC oxidation of the resulting primary alcohol (79%). Finally, differentiation among the three carboxyl groups in 21 (anion formation at C-1, steric congestion at C-16) was observed in the one-step, chemoselective conversion of this intermediate to the requisite keto phosphonate acid 22 (esterification, CSA-MeOH, 97% followed by LiOH hydrolysis, 80% yield based on ca. 75% conversion). The 19R configuration of the reduction product was confirmed by CD studies and by comparisons of materials derived from the starting material (10%) and a monoacetonide (25%, as yet unidentified isomeric structure). (c) 10 equiv of NaBH₄, MeOH, 0 °C, 98%. (d) 0.1 equiv of CSA, MeOH-H₂O (9:1), 0-25 °C, 97%.  (e) 10.0 equiv of 1 N LiOH, HzO, 0-25 °C, 1 h, 80% (75% conversion).

Finally, desilylation of 23 by sequential methylation (CH₂N₂), PDC oxidation, and a second methylation (CH₂N₂) (76% overall yield). The acetate was then removed from 21 (95%) and the carboxylic acid 21 was obtained by PDC oxidation of the resulting primary alcohol (79%). Finally, differentiation among the three carboxyl groups in 21 (anion formation at C-1, steric congestion at C-16) was observed in the one-step, chemoselective conversion of this intermediate to the requisite keto phosphonate acid 22 (esterification, CSA-MeOH, 97% followed by LiOH hydrolysis, 80% yield based on ca. 75% conversion). The 19R configuration of the reduction product was confirmed by CD studies and by comparisons of materials derived from the starting material (10%) and a monoacetonide (25%, as yet unidentified isomeric structure). (c) 10 equiv of NaBH₄, MeOH, 0 °C, 98%. (d) 0.1 equiv of CSA, MeOH-H₂O (9:1), 0-25 °C, 97%.  (e) 10.0 equiv of 1 N LiOH, HzO, 0-25 °C, 1 h, 80% (75% conversion).

The polymeric sulfides of the early transition metals often display interesting magnetic and electrical properties, and have proven to be of considerable importance to many areas, not least of which are heterogeneous catalysis and employment as battery electrodes. A current and important challenge to the synthetic inorganic chemist is the preparation of soluble, discrete counterparts of the polymeric metal–sulfide phases to allow parallel characterization of both the reactivity characteristics and the intrinsic properties of the basic building block of the extended lattice. Such efforts have resulted in considerable progress, particularly in the chemistry of soluble molybdenum sulfides. We herein report the preparation and properties of the first tetranuclear vanadium–sulfur–thiolate species. We believe this complex presages a rich new area of high nuclearity V/S/CR chemistry. In addition, we describe its structural and electronic correspondence to the Li₄VS₂ polymeric phases (0 ≤ x ≤ 1).

Reaction of VCl₄, Li₂S, Na₂edt (edt is ethane-1,2-dithiolate), and NEt₄Br in a 3:4:3:6 ratio in MeCN yields an intensely brown solution that, after filtration and addition of diethyl ether, deposits large black prismatic crystals of [NEt₄]₂[V₄S₂(edt)₆] 2MeCN in analytical purity. A single-crystal structure determination shows the anion (Figure 1) to possess a V₄S₂ central core with two

Reagents and conditions. (a) excess HF-pyr, MeOH, 45 °C, 48 h, 55%. (b) 0.1 equiv of CSA, MeOH, 0-25 °C, 1 h, 50% based on recovered starting material (10%) and a monoacetonide (25%, as yet unidentified isomeric structure). (c) 10 equiv of NaBH₄, MeOH, 0 °C, 98%. (d) 0.1 equiv of CSA, MeOH-H₂O (9:1), 0-25 °C, 97%. (e) 10.0 equiv of 1 N LiOH, HzO, 0-25 °C, 1 h, 80% (75% conversion).
\[ \mu_2\text{-sulfur atoms } S(3) \text{ and } S(3)', \text{ one above and one below an exactly planar } V_4 \text{ parallelogram; the anion possesses an imposed inversion center. Peripheral ligation is accomplished by six } \text{edt}^2 \text{-groups that separate into three types defined by their sulfur binding modes: (i) with both sulfur atoms terminal, } S(12) \text{ and } S(15), (ii) with both sulfur atoms bridging, } S(4) \text{ and } S(7), \text{ and (iii) with one sulfur bridging, } S(8), \text{ and one sulfur terminal, } S(11). \text{ Each type occurs in symmetry-related pairs. The vanadium atoms possess distorted octahedral geometry, and consideration of overall anion charge necessitates the mixed-valence description } V^{III},III,IV,IV. \text{ Based on inspection of structural parameters, however, there is no justification for a trapped-valence description, and the anion is best described as electronically delocalized with an average formal metal oxidation state of } +3.5. \]

The \([V_4S_2]\) core of the \([V_4S_2(\text{edt})_2]^2^-\) anion is very close to representing a discrete portion of the \(Li_VS_2\) phases recently characterized as possessing the layer structure of \(CdI_2\). In \(Li_VS_2\), infinite sheets of octahedrally coordinated vanadium atoms are bridged by \(\mu_2\text{-S}^2^-\) atoms, alternatingly above and below the \(V_4\) plane, with \(Li^+\) ions in interlayer spaces. In \([V_4S_2(\text{edt})_2]^2^-\), effective replacement of peripheral sulfide atoms by thiolate sulfurs keeps the unit discrete and soluble (Figure 2). Thus, with the exception of \(S(7)\) and \(S(7)\), all thiolate sulfur atoms are in positions occupied by \(S^2^-\) atoms in \(VS_2\) which bridge to other metal atoms yielding an infinite lattice. The exception mentioned, \(S(7)\), replaces two \(S^2^-\) atoms of the \(Li_VS_2\) phases that bridge to additional metal centers.

\([V_4S_2(\text{edt})_2]^2^-\) also shows strong similarities to the \(Li_VS_2\) phases by virtue of its variable electron content. The dianion, with its +3.5 average oxidation level, corresponds to \(Li_{10.5}VS_2\) in the cyclic voltammogram, a reversible one-electron oxidation at \(-0.557 \text{ V}\) and two one-electron reductions at \(-1.009\) and \(-1.816 \text{ V}\) (the first reversible) are observed.\(^{10}\) These correspond to other oxidation levels of the \(Li_VS_2\) phases, which have been prepared by varying the Li content (Scheme I; corresponding oxidation levels are presented in the same column).

The accessibility of \([V_4S_2(\text{edt})_2]^{2-}\) cannot be confirmed because the region of the CV at \(>0 \text{ V}\) is masked by a multielectron oxidation wave probably due to ligand oxidation; nevertheless, the overall relationship is clear.

Several examples are known in inorganic chemistry of molecular species that can be considered discrete, soluble fragments of solid-state materials and that display similar variable electron content, but this has not hitherto been the case in metal-sulfide chemistry. The known examples\(^1\) of discrete metal-sulfur aggregates that bear structural relation to polymeric materials either show no reversible redox behavior or, in cases where they do, have no counterpart to such behavior in the solid-state material. The anion \([V_4S_2(\text{edt})_2]^{2-}\) thus represents the first time that such a high degree of correspondence has been established between both the structure and the variable electron content of a solid-state metal-sulfide and its discrete fragment.

The \(Li_VS_2\) phases have been shown to display unusual temperature-dependent magnetic properties and structural distortions as the Li content is varied.\(^5\) Given the potential importance as battery electrodes of this and similar materials such as \(Li_TiS_2\), there is a resulting desire to obtain a deeper understanding of their magnetic, structural, and electronic properties. Availability of discrete structural forms should prove beneficial in allowing the corresponding magnetic, structural, and redox properties of the basic “repeating unit” to be assessed with ease. Such knowledge might be valuable in the future development of these conducting materials. With this in mind, we are currently attempting to isolate the mono- and trionic forms of \([V_4S_2(\text{edt})_2]^2^-\) to allow a parallel study of such properties for three oxidation levels.

Acknowledgment. This work was supported by NSF Grant CHE 8507748.

Supplementary Material Available: Tables of atomic coordinates and isotropic and anisotropic thermal parameters (3 pages). Ordering information is given on any current masthead page.

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(8) The solid-state magnetic moment at 303 K was found to be 2.43 \(\mu_B/\text{V}_4\) unit (1.21 \(\mu_B/\text{V}\), indicating magnetic interactions between the metal centers.

(9) We do not mean to imply by this wording that the sulfur atoms are in exactly the same positions. Note that the coordination geometries of the metal atoms in \([V_4S_2(\text{edt})_2]^2^-\) are severely distorted octahedral, a situation not found in the much higher symmetry of the hexagonal lattice of a \(CdI_2\)-type structure.

(10) Measurements were performed in MeCN solution containing 0.1 M \(\text{Li(N-Bu)}_4\text{ClO}_4\) as supporting electrolyte. Potentials are quoted vs. the normal hydrogen electrode using ferrocene (+0.340 V vs. NHE) as external standard.