vibration in the IR spectra of this bis(macrocycle)barium complex and the equivalence of the hydrogens in the ^1H NMR spectra suggest that the two molecules of the macrocycles are coordinatd in the same way. Indeed the infrared spectra shows a relatively strong band at 1620 cm^{-1} characteristic of the eight coordinated C=N groups. Moreover the ν(P=O) absorption is significantly shifted from 1250 to 1210 cm^{-1} suggesting that Ba^{2+} is also coordinated to the four phosphoryl groups and not to the oxygen of the four furfural moities.

Another synthetic route to complex **4a** has been applied by using metal template procedures. The reaction of the phosphodihydrazide **1** with the furan-2,5-dicarboxaldehyde in the presence of $Ba(ClO_4)_2$ in 2:2:1 molar ratio in methanol at 60 °C gave **4a** (80% yield). An additional complex of Ba(II), having a 2:1 ligand: metal ratio, **5a**, could also be obtained by a metathetical method involving addition of $NaBPh_4$ to the solution of $BaL_2(ClO_4)_2$ in a 1:1 DMF/MeOH solvent mixture.

Interestingly, no complex similar to **4a** is obtained starting either from the thiophosphodihydrazide **1b** ($R = C_6H_5$, $Y = S$), furan-2,5-dicarboxaldehyde, and $Ba(ClO_4)_2$ or from the addition of the barium salt to the macrocycle **3b**. In both cases, the free macrocycle **3b** is formed (or recovered). Studies of the coordination chemistry and chemical properties of macrocycles **3**, **4**, and **5** are under way.

Registry No. **1a**, 54529-67-8; **1b**, 54529-68-9; **1c**, 80182-74-7; **1d**, 56634-20-9; **1e**, 56634-21-0; **2a**, 823-82-5; **2f**, 5431-44-7; **2g**, 626-19-7; **2h**, 623-27-8; **3a**, 116210-65-2; **3b**, 116210-66-3; **3c**, 116210-67-4; **3d**, 116210-68-5; **3e**, 116210-69-6; **3f**, 116210-70-9; **3g**, 116210-71-0; **3h**, 116210-72-1; **4a**, 116232-33-8; **5a**, 116232-34-9; $Ba[ClO_4]_2$, 13465-95-7.

---

(9) Alcock, N. W.; Kingston, R. G.; Moore, P.; Pierpoint, C.; *J. Chem. Soc., Dalton Trans.* **1984**, 1937.

(10) Bailey, N. A.; Eddy, M. M.; Fenton, D. E.; Moss, S.; Mukhopadhyay, A.; Jones, G.; *J. Chem. Soc., Chem. Commun.* **1981**, 628; *J. Chem. Soc., Dalton Trans.* **1984**, 2281.

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$Li_3[VS_4]\cdot 2DMF$: A Solubilized Form of Tetrathiovanadate(V)

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The tetrathiometalates $[VS_4]^{3-}$, $[MoS_4]^{2-}$, $[WS_4]^{2-}$, and $[ReS_4]^{-}$[1] are highly useful starting materials for the preparation of metal sulfide clusters.[2-11] The molybdenum and tungsten anions have been by far the most heavily utilized in this regard.[2-5] They are available as water-soluble ammonium and alkali-metal salts and as quaternary ammonium salts,[12] which have the property of solubility in polar organic solvents where they are stable and can be employed in synthesis, often in homogeneous reaction systems. Recently, $[VS_4]^{3-}$ has been shown to be a precursor to new clusters,[6-11] among which are a fragment of the mineral patronite[7] and those with the cubane-type $[VFe_3(\mu_3\text{-}S)_4]$ core[8] whose vanadium coordination site resembles that in the recently discovered vanadium-containing nitrogenases.[13] Results such as these presage substantial exploitation of $[VS_4]^{3-}$ in synthesis.

Tetrathiovanadate(V) was first prepared in 1890–1891[14] as its ammonium salt by the prolonged reaction of NH_4VO_3 with H_2S in strongly ammoniacal solution. An improved modification of this synthesis has been reported.[6] The compound is soluble in strongly alkaline aqueous solution where the anion has limited stability. The salt is somewhat soluble in DMF and Me_2SO but rapidly changes color in these solvents. While $(NH_4)_3[VS_4]$ has been used successfully as a synthetic precursor in heterogeneous nonaqueous[6,8,10] and aqueous/nonaqueous[11] systems and in aqueous solution,[15] it is clearly desirable to have a salt that is soluble in aqueous solution and in those more polar nonaqueous solvents commonly employed in synthesis. The lithium salt fulfills this requirement; its synthesis and properties are reported here. In the interim from the initial preparation of $(NH_4)_3[VS_4]$, no other synthetically useful salt has been isolated.

Experimental Section

Preparation of $Li_3[VS_4]\cdot 2DMF$. DMF (Burdick & Jackson) was dried over 4-Å molecular sieves and degassed before use; Li_2S (Cerac) was used as received. All operations were performed under a pure dinitrogen atmosphere. Lithium sulfide (1.50 g, 33 mmol) and $(NH_4)_3[VS_4]$[6] (5.00 g, 20 mmol) were added to 500 mL of dry DMF. The slurry was stirred at room temperature under dynamic vacuum for 2 days. The oily residue was thoroughly washed with dry degassed THF. The purple solid was collected by filtration and dried in vacuo. ^{51}V NMR (Me_2SO): 1388 ppm [lit.[16] 1395 ppm (aqueous)]. Absorption spectrum (Me_2SO), λ_{max} (ϵ_M): 353 (8930), 396 (6130), 523 (6510), 560 (sh, 5370) nm. Anal. Calcd for $C_6H_{14}Li_3N_2O_2S_4V$: C, 20.82; H, 4.08; Li, 6.01; N, 8.09; S, 37.05; V, 14.71. Found: C, 21.48; H, 4.22; Li, 5.93; N, 8.49; S, 36.55; V, 15.80.

Physical Measurements. NMR measurements were made with a Bruker WM-300 spectrometer under the following conditions: ^7Li, 116.679 MHz, 100–320 scans, saturated LiCl in D_2O as external reference; ^{51}V, 78.906 MHz, 2000–5000 scans, pure $VOCl_3$ as external reference. NMR and absorption spectra were determined under strictly anaerobic conditions.

Results and Discussion

When dissolved in strongly basic aqueous solutions, $(NH_4)_3[VS_4]$ initially forms a deep red-violet solution. Such solutions tend to develop a brown color, with the rate of color change being faster as the pH is decreased below ca. 14. When this compound is dissolved in DMF or Me_2SO, the solution immediately turns brown and shortly thereafter generates a nearly featureless absorption spectrum. Thus, a 9 mM solution in Me_2SO, after 5 min exhibited maxima at 336, 496, and 660 nm, the spectrum being completely different from that of authentic $[VS_4]^{3-}$ (vide infra). When monitored over 24 h the solution evidenced further spectral changes, with the final spectrum consisting of a weak band at 490 nm and a stronger band at 300 nm. Similarly, a saturated solution of $(NH_4)_3[VS_4]$ in DMF examined after 4 h afforded a ^{51}V NMR spectrum consisting of no less than six signals of varying intensities (at 985, 1000, 1009, 1013, 1046, and 1343 ppm). None of these signals arises from $[VS_4]^{3-}$.

Accompanying the development of a brown color when $(NH_4)_3[VS_4]$ is dissolved in DMF or Me_2SO is a strong odor of ammonia. When volatiles are pumped off, an intractable black solid separates from a colorless solution. These observations imply that, under these conditions, $[VS_4]^{3-}$ is a stronger base than NH_3

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(1) Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934.

(2) Holm, R. H. *Chem. Soc. Rev.* **1981**, *10*, 455.

(3) Coucouvanis, D. *Acc. Chem. Res.* **1981**, *14*, 201.

(4) Holm, R. H.; Simhon, E. D. In *Molybdenum Enzymes*; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1985; Chapter 1.

(5) Müller, A. *Polyhedron* **1986**, *5*, 323.

(6) Do, Y.; Simhon, E. D.; Holm, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 6731; *Inorg. Chem.* **1985**, *24*, 4635.

(7) Halbert, T. R.; Hutchings, L. L.; Rhodes, R.; Stiefel, E. I. *J. Am. Chem. Soc.* **1986**, *108*, 6437.

(8) Kovacs, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 340; *Inorg. Chem.* **1987**, *26*, 702, 711.

(9) Kovacs, J. A.; Bashkin, J. K.; Holm, R. H. *Polyhedron* **1987**, *6*, 1445.

(10) Scattergood, C. D.; Bonney, P. G.; Slater, J. M.; Garner, C. D.; Clegg, W. *J. Chem. Soc., Chem. Commun.* **1987**, 1749.

(11) Müller, A.; Schimanski, J.; Bögge, H.; *Z. Anorg. Allg. Chem.* **1987**, *544*, 107.

(12) McDonald, J. W.; Freisen, G. D.; Rosenhein, L. D.; Newton, W. E. *Inorg. Chim. Acta* **1983**, *72*, 205.

(13) (a) Arber, J. M.; Dobson, B. R.; Eady, R. R.; Stevens, P.; Hasnain, S. S.; Garner, C. D.; Smith, B. E. *Nature (London)* **1987**, *325*, 372. (b) Smith, B. E.; Eady, R. R.; Lowe, D. J.; Gormal, C. *Biochem. J.* **1988**, *250*, 299.

(14) Krüss, G.; Ohnmais, K. *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 2547; *Justus Liebigs Ann. Chem.* **1891**, *263*, 39.

(15) Müller, A.; Krickemeyer, E.; Penk, M.; Walberg, H. J.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1045.

(16) Harrison, A. T.; Howarth, O. W. *J. Chem. Soc., Dalton Trans.* **1986**, 1405.

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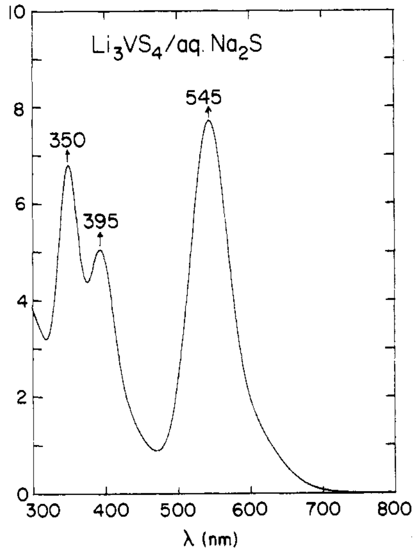

Figure 1. UV/visible absorption spectrum of 17 mM $Li_3[VS_4]\cdot 2DMF$ in saturated aqueous sodium sulfide solution.

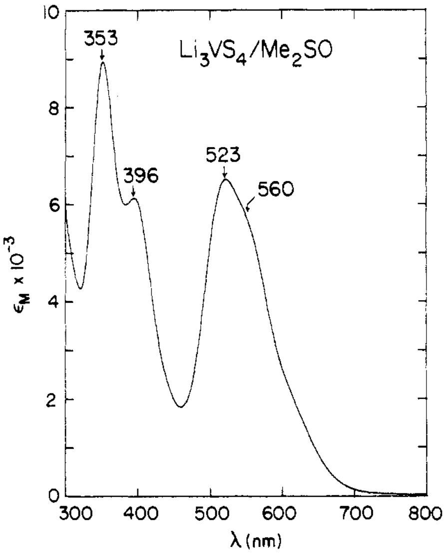

Figure 2. UV/visible absorption spectrum of 10 mM $Li_3[VS_4]\cdot 2DMF$ in Me_2SO solution.

and that any protonated version of the former probably decomposes to polymeric vanadium sulfides with likely evolution of H_2S. They further indicate that, in order to stabilize $[VS_4]^{3-}$ in a nonaqueous solvent, NH_4^+ should be removed and the S:V atom ratio maintained at 4:1. The reaction

$$(NH_4)_3[VS_4] + 1.5Li_2S \rightarrow Li_3[VS_4] + 1.5H_2S + 3NH_3$$

meets these requirements and was used in the synthesis. Here additional sulfide is provided to compensate for that presumably lost as H_2S. All byproducts are gaseous, thereby simplifying product isolation. In conducting the preparation, it is important that the reaction mixture be maintained under dynamic vacuum for no less than 2 days in order to remove all of the volatile byproducts.

The product was obtained as a noncrystalline purple solid which, from analytical results, is formulated as a bis(dimethylformamide) solvate. DMF was observed in the ^1H NMR spectrum. Loss of solvate may account for the slightly high metal analysis obtained in this laboratory. $Li_3[VS_4]\cdot 2DMF$ is freely soluble, is entirely stable in dry anaerobic polar solvents such as DMF and Me_2SO, and is insoluble in acetonitrile, dichloromethane, and THF, among the solvents tested. Solution properties are essentially the same in the first two solvents; the behavior in Me_2SO is briefly considered.

The UV/visible spectrum of $Li_3[VS_4]\cdot 2DMF$ in aqueous sodium sulfide solution, where the anion is particularly stable under anaerobic conditions, is shown in Figure 1. The solution is red-purple, and the spectrum is indistinguishable from that in 1 M NaOH,[6,17] thus assuring that the product contains authentic $[VS_4]^{3-}$. The spectrum in Me_2SO, set out in Figure 2, contains the same three-band system as in aqueous solution but with changes in relative intensities and a splitting of the visible band into two partially resolved features. The ^{51}V chemical shift (1388 ppm) is within 7 ppm of that of $[VS_4]^{3-}$ in aqueous solution, which in turn is well separated from that of the first hydrolysis product, $[VOS_3]^{3-}$ (740 ppm), and from $[V_2S_7]^{4-}$ (1457 ppm).[16] The ^7Li NMR spectrum of the compound in Me_2SO-d_6 shows a signal at 1.76 ppm, shifted 0.7 ppm downfield compared to the spectrum of LiCl in the same solvent at the same concentration. Further, under these conditions, the half-height width of the signal in the solution prepared from the lithium salt is 80 Hz vs 2 Hz for LiCl. The collective observations indicate that Me_2SO and DMF solutions prepared from $Li_3[VS_4]\cdot 2DMF$ contain the $[VS_4]^{3-}$ ion, which is presumably stabilized by interactions with solvated Li^+. These interactions presumably contribute to the differences in aqueous and nonaqueous absorption spectra. Given that the spectra arise from LMCT transitions, it is not surprising that they are subject to perturbations by extrinsic factors. The low-energy band is likely $^1A_1 \rightarrow {}^1T_2$[18] and thus is subject to splitting.

When $Li_3[VS_4]\cdot 2DMF$ in Me_2SO solution is treated with 1 equiv of either acetic acid or HBF_4 etherate, the solution immediately turns brown. Its ^{51}V NMR spectrum shows the presence of one species, with a chemical shift of 1343 ppm. This does not closely match any signal in aqueous solution,[16] but might be from putative $[VS_3(SH)]^{2-}$ (claimed at 1392 ppm in water[16]). Addition of 2 equiv affords a signal at 991 ppm and subsequent formation of a black solid. These observations further emphasize the sensitivity of $[VS_4]^{3-}$ to protic species.

Lastly, other forms of $[VS_4]^{3-}$ have been reported. The mineral sulvanite (Cu_3VS_4) contains this entity[19] as does Tl_3VS_4,[20] but covalent cation–sulfur binding in infinite lattices renders these compounds intractable. The sodium[16] and potassium[21] salts been prepared from the elements at high temperature. The former is soluble in water and has been used in NMR experiments.[16] Halbert et al.[7] have generated the soluble tricaprylylmethylammonium salt[22] from $[(n\text{-}C_8H_{17})_3MeN]Cl$ and $(NH_4)_3[VS_4]$ in situ in toluene containing 2% DMF. This should be a useful procedure for nonpolar solvents, especially when the synthetic product sought is a neutral compound. Salts of $(n\text{-}C_8H_{17})_3MeN^+$ are likely to prove difficult to crystallize. We have been unable to isolate demonstrably pure quaternary cation salts of $[VS_4]^{3-}$. The compound reported here and the means of generating quaternary salts in nonpolar media should substantially enhance the utility of tetrathiovanadate(V) ion in reaction chemistry.

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(17) Vogler, A.; Kunkely, H. *Inorg. Chem.* **1988**, *27*, 504.

(18) Müller, A.; Diemann, E.; Ranade, A. C. *Chem. Phys. Lett.* **1969**, *3*, 467.

(19) Pauling, L.; Hultgren, R. *Z. Kristallogr., Kristallgeom., Kristallphys., Krystallchem.* **1933**, *84*, 204.

(20) Crevecoeur, C. *Acta Crystallogr.* **1964**, *17*, 757.

(21) Omloo, W. P. F. A. M.; Jellinek, F. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 1205.

(22) The spectrum of this salt is reported also as a three-band system.[7] The substantial energy shifts (λ_{max} = 326, 364, and 538 nm) compared to the spectra in Figures 1 and 2 are apparently another manifestation of medium effects on the spectrum of $[VS_4]^{3-}$.