in $[(CO)_8Fe_2$-μ-C=C$(C_6H_5)_2]$,[7] and already 112.4° in C_2F_4.[10] In the difluorovinylidene complex the F-C-F angle is even smaller, 106.2°.

Experimental Section

Material. Difluoromalonyl dichloride[11] and triiron undecacarbonylate[12] were obtained by literature procedures.

Synthesis of $[(CO)_8Fe_2(\mu$-C=$CF_2)]$. Under anhydrous and oxygen-free conditions difluoromalonyl dichloride (0.84 g, 48 mmol), dissolved in a few milliliters of THF, is slowly added at −78 °C to a freshly prepared solution of 2.3 g (4.8 mmol) $[Fe_3(CO)_{11}]^{2-}$ in 50 mL of THF. Warming to −50 °C led to evolution of gas. At room temperature the solvent is pumped off to dryness. The solid residue is sublimed at 70 °C in vacuum onto a −30 °C finger, giving a yellow sublimate and a black residue. Chromatography of the yellow sublimate in CH_2Cl_2/pentane (1:3) on silica gel affords 0.47 g of pure $[(CO)_8Fe_2(\mu$-C=$CF_2)]$ in 25% yield.

IR (solid in KBr): ν_{CO} 2117, 2068, 2039, 2022 cm^{-1}; ν_{CC} 1698 cm^{-1}; mass spectrum: m/z 398 (M^+), and smaller fragments, mainly due to subsequent loss of CO. ^{19}F NMR (CH_2Cl_2): δ = −68.8.

Crystal Structure Analysis. An orange crystal of about 0.2 mm size in all dimensions was obtained from recrystallization in pentane, and mounted on a Siemens diffractometer using Mo Kα radiation (λ = 71.06 pm) and a graphite monochromator at room temperature.

Crystal data: space group $P2_1/n$, a = 700.9 (3) pm, b = 1307.4 (7) pm, c = 1504.3 (6) pm, β = 96.10 (3)°, Z = 4, ρ_{calcd} = 1.93 g cm^{-3}, 2500 measured reflections up to 2θ = 50° ($\pm h,k,l$), 2180 reflections with $I > 2\sigma(I)$, 200 parameters. The structure was solved with the program SHELX; the scattering factors were taken from the *International Tables for X-Ray Crystallography*. The function $\sum w(|F_o| - |F_c|)^2$ was minimized. Absorption correction: numerical, μ = 22.5 cm^{-1}. Extinction correction: isotropic, $g = 5.5 \times 10^{-4}$. Weighing scheme: $w = 1.7291 - 0.822F + 0.0002F^2 - 0.0000066F^3$. R = 0.037, R_w = 0.036.

Acknowledgment is expressed to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie and also to Du Pont, Wilmington, DE, for a gift of $Na_2[CF_2(COO)_2]$.

Supplementary Material Available: Complete listings of anisotropic thermal parameters, bond lengths, and bond angles (3 pages); a table of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

(11) Fear, E. J. P.; Thrower, J.; Veitch, J. *J. Chem. Soc.* **1956**, 3199.
(12) Strong, H.; Krusic, P. J.; Filippo, J. S. *Inorg. Synth.* **1986**, *24*, 157.

Contribution from the Laboratoire de Synthèse, Structure et Réactivité de Molécules Phosphorées, UA No. 454, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex, France, and Laboratoire de Chimie des Agroressources, Institut National Polytechnique de Toulouse, Ecole Nationale Supérieure de Chimie de Toulouse, 118 route de Narbonne, 31077 Toulouse Cedex, France

Facile Synthesis of New Classes of Free and Complexed Polyaza Phosphorus Macrocycles

Jean-Pierre Majoral,*[†] Meryam Badri,[†] Anne-Marie Caminade,[†] Michel Delmas,[‡] and Antoine Gaset[‡]

Received February 11, 1988

Binucleating macrocyclic ligands have been the subject of intensive studies.[1] In particular phosphorus macrocycles possessing P-C,[2] P-O, or P-S[3] bonds have been the focus of much attention since these derivatives can react as hard or soft chelating units depending of the hybridization of the phosphorus atoms. In contrast very few reports deal with the preparation of azaphospha macrocycles,[4] and to our knowledge no similar work has been devoted to the synthesis of bis(phosphodihydrazino) macrocycles derived from heterocyclic dicarbonyls. Here we describe the high-yield one-pot synthesis of the first 20- and 22-membered ring macrocycles possessing P-N-N linkages, as well as the preparation of related complexes.

Experimental Section

All experiments were performed under an atmosphere of dry argon or nitrogen. Melting points are uncorrected. ^{1}H NMR spectra were recorded on a Bruker WM 250 or a Bruker AC 80 spectrometer. ^{1}H chemical shifts are reported in ppm relative to Me_4Si as internal standard. ^{31}P and ^{11}B NMR spectra were obtained on a Bruker AC 80 instrument and are reported in ppm. Standards for the shifts are 85% H_3PO_4 and $BF_3O(C_2H_5)_2$ for phosphorus and boron, respectively. Infrared spectra were recorded on a Perkin-Elmer 225 instrument. Mass spectra were obtained on a Varian MAT 311A instrument.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and must be handled with great caution.[5]

Synthesis of Macrocycles 3a-h. A solution of phosphodihydrazides, **1**[6] (0.02 mol), in 50 mL of methanol and a solution of dialdehydes, **2** (0.02 mol), in 50 mL of methanol are added simultaneously and dropwise at room temperature over a period of 1 h. The mixture is stirred for 2 h, during which a yellow precipitate is formed. The solution is filtered and the precipitate washed with 2 × 20 mL of methanol and recrystallized from acetonitrile/chloroform 4:1. An additional amount of macrocycles **3** is obtained by evaporation of methanol and recrystallization of the residue from acetonitrile/chloroform 4:1.

3a: yellow powder; yield 85%; mp, dec >180 °C. ^{31}P NMR ($CDCl_3$): 23.90. ^{1}H NMR ($CDCl_3$): 3.0 (d, $^3J_{PH}$ = 7 Hz, N—CH_3) 6.40 (s, C_4OH_2) 7.4 (m, C_6H_5) 7.9 (s, HC=N-). ^{13}C NMR ($CDCl_3$): 31.54 (d, $^2J_{PC}$ = 7.85 Hz), 110.78 (s, *C*—C—O furfural), 132.59 (s, C—*C*—O furfural), 128.30 and 133.48 (m, C_6H_5), 151.92 (s, *C*=N). IR (KBr) 1660 (C=N), 1250 (P=O). MS: m/e 604. Anal. Calcd for $C_{28}H_{30}N_8O_4P_2$: C, 55.62; H, 4.96; N, 18.54. Found: C, 55.26; H, 4.98; N, 18.50.

3b: yellow powder; yield 95%; mp, dec >180 °C. ^{31}P NMR ($CDCl_3$): 78.73. ^{1}H NMR ($CDCl_3$): 3.08 (d, $^3J_{PH}$ = 9.1 Hz, N—CH_3), 6.33 (s, C_4OH_2), 7.34 (m, C_6H_5) 8.08, (s, HC=N-). ^{13}C NMR ($CDCl_3$) 31.78 (d, $^2J_{PC}$ = 8.66 Hz), 111.10 (s, C—*C*—O furfural), 132.23 (s, *C*—C—O furfural), 128 and 134.19 (m, C_6H_5), 151.67 (s, *C*=N-). IR (KBr): 1670 (C=N), 730 (P=S) cm^{-1}. MS: m/e 636. Anal. Calcd for $C_{28}H_{30}N_8O_2P_2S_2$: C, 52.84; H, 4.71; N, 17.61. Found: C, 52.43; H, 4.82; N, 17.28.

3c: yellow powder; yield 75%; mp, dec >150 °C. ^{31}P NMR ($CDCl_3$): 1.40. ^{1}H NMR ($CDCl_3$): 3.2 (d, $^3J_{PH}$ = 6.92 Hz, N—CH_3), 6.50 (s, C_4OH_2), 7.2 (m, C_6H_5), 7,4 (s, *H*C=N). IR (KBr): 1670 (C=N), 1270 (P=O) cm^{-1}. MS: m/e 636. Anal. Calcd for $C_{28}H_{30}N_8O_6P_2$: C, 52.83; H, 4.71; N, 17.61. Found: C, 52.51; H, 4.61; N, 17.51.

[†] Université Paul Sabatier.
[‡] Ecole Nationale Supérieure de Chimie de Toulouse.

(1) See, for example: Fenton, D. E. *Pure Appl. Chem.* **1986**, *11*, 1437 and references included therein.
(2) See, for example: (a) Riker-Nappier, J.; Meek, D. W. *J. Chem. Soc., Chem. Commun.* **1974**, 442. (b) Cabral, O.; Cabral, M. F; Drew, M. G. B.; Nelson, S. M.; Rodgers, A. *Inorg. Chim Acta* **1977**, *25*, L77. (c) Newkome, G. R.; Hager, D. C. *J. Am. Chem. Soc.* **1978**, *100*, 5567. (d) Del Donno, T. A.; Rosen, W. *Inorg. Chem.* **1978**, *12*, 3714. (e) Kaplan, L. J.; Weisman, G. R.; Cram, D. J. *J. Org. Chem.* **1979**, *13*, 2226. (f) Christol, H.; Cristau, H. J.; Fallouh, F.; Hullot, P. *Tetrahedron Lett.* **1979**, *28*, 2591. (g) Ciampolini, M.; Dapporto, P.; Nardi, N.; Zanobini, F. *J. Chem. Soc., Chem. Commun.* **1980**, 177. (h) Fox, M. A.; Campbell, K. A.; Kyba, E. P. *Inorg. Chem.* **1981**, *20*, 4163. (i) Ciampolini, M.; Dapporto, P.; Dei, A.; Nardi, N.; Zanobini, F. *Inorg. Chem.* **1982**, *21*, 489. (j) Ciampolini, M.; Dapporto, P.; Nardi, N.; Zanobini, F. *Inorg. Chem.* **1983**, *22*, 13. (k) Bartsch, R.; Hietkamp, S.; Peters, H.; Stelzer, O. *Inorg. Chem.* **1984**, *23*, 3304. (l) Kyba, E. P.; Clubb, C. N.; Larson, S. B.; Schueler, V. J.; Davis, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 2141. (m) Ansell, C. W. G.; Cooper, M. K.; Dancey, K. P.; Duckworth, P. A.; Henrick, K.; McPartlin, M.; Tasker, P. A. *J. Chem. Soc., Chem. Commun.* **1985**, 439. (n) Wei, L.; Bell, A.; Warner, S.; Williams, I. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1986**, *108*, 8302. (o) Vincens, M.; Grimaldo Moron, J. T.; Pasqualini, R.; Vidal, M. *Tetrahedron Lett.* **1987**, *28*, 1259 and references included therein.
(3) (a) Albrand, J. P.; Dutasta, J. P.; Robert, J. B. *J. Am. Chem. Soc.* **1974**, *96*, 4584. (b) Dutasta, J. P.; Grand, A.; Guimaraes, A. C.; Robert, J. B. *Tetrahedron Lett.* **1979**, *35*, 197. (c) Kirsanov, A. V.; Kudrya, T. N.; Shtepanek, A. S. *Zh. Obshch. Khim.* **1980**, *50*, 2452 and references included therein.
(4) (a) Grandjean, J.; Laszlo, P.; Picavet, J. P.; Sliwa, J. P. *Tetrahedron Lett.* **1978**, 1861. (b) Chivers, T.; Sudheendra Rao, M. N.; Richardson, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 702. (c) Hope, H.; Viggiano, M.; Moezzi, B.; Powder, P. P. *Inorg. Chem.* **1984**, *23*, 2550.
(5) (a) Steere, N. V. *J. Chem. Educ.* **1973**, *50*, A335. (b) Raymond, K. N. *Chem. Eng. New* **1983**, *61* (Dec 5), 4.
(6) Majoral, J.-P.; Kraemer, R.; Navech, J.; Mathis, F. *Tetrahedron* **1976**, *32*, 2633 and references therein.

0020-1669/88/1327-3873$01.50/0

3d: yellow powder; yield 80%; mp, dec >150 °C. ^{31}P NMR ($CDCl_3$): 67.0. ^1H NMR ($CDCl_3$): 3.1 (d, $^3J_{PH}$ = 9.5 Hz, N—CH_3), 6.5 (s, C_4OH_2), 7.5 (m, C_6H_5, HC=N-). IR (KBr): 1670 (C=N), 775 (P=S) cm^{-1}. MS: *m/e* 668. Anal. Calcd for $C_{28}H_{30}N_8O_4P_2S_2$: C, 50.29; H, 4.49; N, 16.76. Found: C, 50.01; H, 4.29; N, 16.52.

3e: yellow powder; yield 85%; mp dec >200 °C. ^{31}P NMR ($CDCl_3$): 18.2. ^1H NMR ($CDCl_3$): 2.8 (d, $^3J_{PH}$ = 10 Hz, $N(CH_3)_2$), 3.1 (d, $^3J_{PH}$ = 8 Hz), 6.53 (s, C_4OH_2), 7.43 (s, HC=N); ^{13}C NMR ($CDCl_3$): 32.23 (d, $^2J_{PC}$ = 7.85 Hz, N—N—CH_3), 37.6 (d, $^2J_{PC}$ = 2.82 Hz, $N(CH_3)_2$), 110.36 (s, C—C—O furfural), 127.2 (s, C—C—O furfural), 151.7 (s, C=N). IR (KBr): 1665 (C=N), 1240 (P=O) cm^{-1}. MS: *m/e* 538. Anal. Calcd for $C_{20}H_{32}N_{10}O_4P_2$: C, 44.60; H, 5.94; N, 26.02. Found: C, 44.28; H, 6.32; N, 25.78.

3f: white powder; yield 85%; mp, dec >220 °C. ^{31}P NMR ($CDCl_3$): 78.4. ^1H NMR ($CDCl_3$): 3.3 (d, $^3J_{PH}$ = 9 Hz, N—CH_3), 7.4 and 8 (C_5NH_3 and C_6H_5). ^{13}C NMR ($CDCl_3$): 32.12 (d, $^2J_{PC}$ = 10 Hz), 152.18 (s, C=N). IR (KBr): 1590 (C=N), 880 (P=S) cm^{-1}. MS: *m/e* 658. Anal. Calcd for $C_{30}H_{32}N_{10}P_2S_2$: C, 54.71; H, 4.86; N, 21.27. Found: C, 54.08; H, 4.74; N, 20.67.

3g: white powder; yield 40%; mp, dec >215 °C. ^{31}P NMR ($CDCl_3$): 78.2. ^1H NMR ($CDCl_3$): 3.1 (d, $^3J_{PH}$ = 9.4 Hz, NCH_3), 7.4 (s, HC=N), 7.5 and 7.9 (m, C_6H_4 and C_6H_5). ^{13}C NMR ($CDCl_3$): 31.43 (d, $^2J_{PC}$ = 9.67 Hz), 125–135 (m, C_6H_3 and C_6H_5), 136.21 (C=N). IR (KBr): 1595 (C=N), 720 (P=S) cm^{-1}. MS: *m/e* 656. Anal. Calcd for $C_{32}H_{34}N_8P_2S_2$: C, 58.53; H, 5.18; N, 17.07. Found: C, 57.98; H, 5.26; N, 16.48.

3h: white powder, yield 50%; mp, dec >215 °C. ^{31}P NMR ($CDCl_3$): 78.2. ^1H NMR ($CDCl_3$): 3.2 (d, $^3J_{PH}$ = 9.6 Hz, NCH_3), 7.4 and 8 (m, C_6H_4 and C_6H_5). ^{13}C NMR ($CDCl_3$) 31.43 (d, $^2J_{PC}$ = 9.67 Hz, N—CH_3), 136.10 s, C=N). IR (KBr) 1590 (C=N), 720 (P=S) cm^{-1}. MS: *m/e* 656. Anal. Calcd for $C_{32}H_{34}N_8P_2S_2$: C, 58.53; H, 5.18; N, 17.07. Found: C, 57.72; H, 5.40; N, 17.03.

Synthesis of the Complex $[BaL_2][(ClO_4)_2]$ (4a). Method A. To a solution of the macrocycle **3a** (0.604 g, 1 mmol) in 10 mL of methanol/chloroform (1:1) is added dropwise a solution of barium perchlorate (0.167 g, 0.5 mmol) in 5 mL of methanol/chloroform (1:1), at room temperature. **4a** precipitates as soon as it is formed. The mixture is stirred for 1 h and the orange precipitate washed with 2 × 5 mL of methanol.

Method B (Template Reaction). A mixture of 2,5-furandicarboxaldehyde (0.992 g, 8 mmol), phosphodihydrazide **1a** (1.712 g, 8 mmol), and barium perchlorate (0.672 g, 2 mmol) is dissolved in refluxing methanol (200 mL). An orange precipitate quickly appears. The mixture is stirred for 1 h, and the solid is filtered and washed with 2 × 10 mL of methanol. **4a** is recrystallized in dimethylformamide/methanol 1:2.

4a: yield 80%. ^{31}P NMR (DMF): 23.3. ^1H NMR (DMSO): 3.0 (d, $^3J_{PH}$ = 6.7 Hz, NCH_3), 6.56 (s, C_4OH_2), 7.6 (m, C_6H_5, H—C=N). IR (KBr): 1620 (C=N), 1210 (P=O), 1090, 620 (ClO_4) cm^{-1}. Anal. Calcd for $C_{56}H_{60}N_{16}Cl_2O_{16}P_4Ba$: C, 43.51 H, 3.88; N, 14.50; Cl, 4.59. Found: C, 42.85; H, 4.13; N, 13.28; Cl, 4.34.

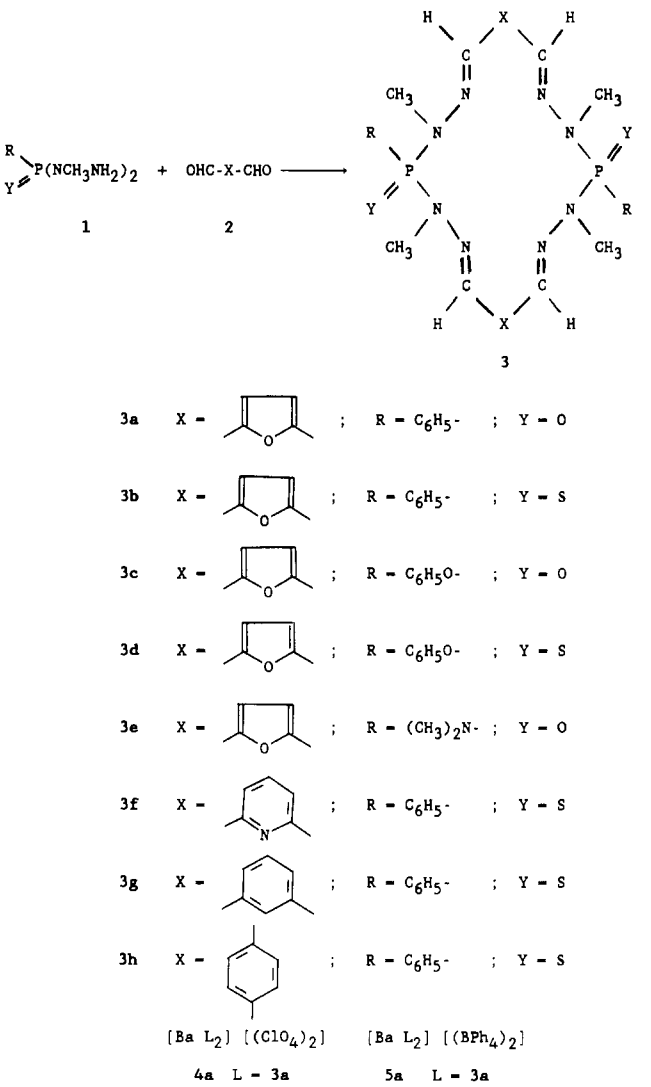
Synthesis of the Complex $[BaL_2][(BPh_4)_2]$ (5a). To a solution of the complex **4a** (0.5 g, 0.32 mmol) in 10 mL of dimethylformamide/methanol (1:1) is added dropwise at room temperature $NaBPh_4$ (0.22 g, 0.64 mmol) in 10 mL of the same mixture of solvents. The resulting mixture is heated at 70 °C for 2 h. The solvents are evaporated and the residue washed several times with methanol and recrystallized as a brown powder from dimethylformamide/methanol (1:2).

5a: yield 60%. ^{31}P NMR (DMF): 23.27. ^{11}B NMR (DMF/C_6D_6): -7.06. ^1H NMR (DMSO): 2.99 (d, $^3J_{PH}$ = 6.84 Hz, N—CH_3), 6.54 (s, C_4OH_2), 7.24 (m, P—C_6H_5, H—C=N, B—C_6H_5). IR (KBr): 1620 (C=N) 1200 (P=O) cm^{-1}. Anal. Calcd for $C_{80}H_{80}N_{16}O_8P_4BBa$: C, 62.9; H, 5.04; N, 11.29. Found: C, 60.26; H, 4.94; N, 11.02.

Results and Discussion

In general, template procedures are necessary for the preparation of [2 + 2] macrocycles derived from heterocyclic dicarbonyls.[1,7] However stable macrocycles **3a–g** (20-membered ring) and **3h** (22-membered ring) can be formed in excellent yield when a solution of phosphodihydrazides **1** in methanol and a solution of the dialdehydes **2** in methanol are added simultaneously and dropwise at room temperature (Scheme I). All the compounds precipitated as soon as they are generated except for **3e**, which is soluble in methanol. Their structures were deduced from ^{31}P, ^1H, and ^{13}C NMR, IR, and mass spectroscopies as well as

Scheme I



microanalysis. Indeed the IR spectra showed the 1670–1660-cm^{-1} bands characteristic of the C=N groups. None of the spectra exhibited any absorption at 3250–3400 or at ca. 1700 cm^{-1} that could be attributed to unreacted hydrazine or carbonyl functions. Moreover the ^{13}C NMR spectra is fully consistent with the presence of imine carbon atoms. The formation of the N=CH– moities is further confirmed by a singlet at low field (from 7.4 to 8.08 ppm) in the ^1H NMR spectra. Mass spectrometry (field desorption) as well as cryoscopic measurements confirm the [2 + 2] condensation reaction.

Compounds **3** are not sensitive to hydrolysis, and unexpectedly no cleavage of the intracyclic phosphorus–nitrogen bond was detected when **3a–h** were treated with hydrogen chloride or hydrogen fluoride even under drastic conditions! Furthermore, desulfuration of **3b**, **3d**, **3f**, and **3g** with *n*-butylphosphine failed.

A stable complex **4a** is nearly quantitatively obtained when the macrocycle **3a** (2 equiv) in THF and the salt $Ba(ClO_4)_2$ (1 equiv) in the same solvent were simultaneously mixed at room temperature. **4a** is isolated as a yellow powder (85% yield) and characterized by its spectroscopic data and elemental analysis indicating a 2:1 macrocycle:metal stoichiometry.

Although no suitable crystals for an X-ray study could be formed, coumpound **4a** may be described as a 12-coordinate Ba^{2+} "sandwich" complex $[BaL_2][ClO_4^-]_2$ (L = **3a**) by analogy with a related 18-membered conjugated tetraimino macrocyclic complex described by Nelson et al.[8] The occurrence of one ν(C=N)

(7) A few unstable free macrocycles were obtained for example by reacting 2.6 diacetylpyridine with bis(aminopropyl)amine[9] or thiophene-2,5-dicarbaldehyde with primary amine.[10]

(8) Nelson, S. M.; Esho, F. S.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* **1983**, 1857.

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.

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

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

Yi-ping Zhang and R. H. Holm*

Received June 3, 1988

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

(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.

0020-1669/88/1327-3875$01.50/0