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Synthesis and Coordination Chemistry of (Carbamoylmethyl)thiophosphonates. Crystal and Molecular Structure of *cis*-Dioxodichlorobis[diethyl ((diethylcarbamoyl)methyl)thiophosphonate]molybdenum(VI)

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Bifunctional (carbamoylmethyl)thiophosphonates, $(RO)_2P(S)CH_2C(O)NEt_2$ (R = Et, Bu), have been prepared and characterized by elemental analyses and mass, infrared, and NMR spectroscopy. The coordination chemistry of one ligand (R = Et) with molybdenyl, lanthanide, and uranyl ions has been surveyed. *cis*-Dioxodichlorobis[diethyl ((diethylcarbamoyl)methyl)thiosphosphonate]molybdenum(VI), $MoO_2Cl_2[(C_2H_5O)_2P(S)CH_2C(O)N(C_2H_5)_2]_2$, has been isolated from the combination of MoO_2Cl_2 and the thiophosphonate ligand in ethanol/ether mixtures. The resulting complex has been characterized by elemental analyses, infrared and ^{31}P and ^{13}C NMR spectroscopy, and single-crystal X-ray diffraction analysis. The complex was found to crystallize in the monoclinic space group $C2/c$ with $a = 12.473$ (4) Å, $b = 15.191$ (7) Å, $c = 17.951$ (6) Å, $\beta = 95.87$ (3)°, $Z = 4$, $V = 3383.5$ (9) Å^3, and $\rho_{calcd} = 1.44$ g cm^{-3}. The structure was solved by heavy-atom methods, and blocked least-squares refinements converged at $R_F = 5.6\%$ and $R_{wF} = 5.9\%$ on 2670 unique reflections with $F \geq 5\sigma(F)$. The structure contains monomeric units of the complex with the six-coordinate Mo atom having a pseudooctahedral coordination geometry. The two (carbamoylmethyl)thiophosphonate ligands are bonded to the Mo atom in a monodentate mode through the carbonyl oxygen atoms. Several important bond distances are Mo—O(oxo)$_{av}$ = 1.702 (4) Å, Mo—CO$_{av}$ = 2.368 (1) Å, Mo—O(carbonyl) = 2.234 (3) Å, P=S = 1.921 (2) Å, and C=O = 1.265 (5) Å.

Introduction

Phosphonates, $(RO)_2R'PO$, phosphine oxides, R_3PO, and carbonyls, R_2CO, are known to form a large variety of neutral ligand coordination complexes with hard/"class a" metal ions.[1] The coordination chemistry of analogous thiophosphonates, $(RO)_2R'PS$, phosphine sulfides, R_3PS, and thiocarbonyls, R_2CS, is less thoroughly developed; however, it is generally found that these ligands prefer to bind with soft/"class b" metal ions.[1,2] These differences have led to the application of these ligands in several useful metal ion separation schemes,[3] and they have inspired the design and syntheses of several bifunctional ligands containing both hard and soft donor sites. For example, β-diketones are well-known ligands that bind most hard metal ions and some intermediate and soft metal ions with the anionic (β-diketonate) form of the ligand and in a bidentate coordination mode.[3,4] Substitution of both carbonyl functions with thiocarbonyl groups results in dithio β-diketones, which also normally bind as anionic ligands with soft metal ions.[4] Monothio β-diketone ligands, $RC(O)CH_2C(S)R'$, show varied coordination chemistry, but the dominant coordination mode is still with the anionic form of the ligand.[4-6] Although some use has been made of the β-diketonates in laboratory metal ion separations, few attempts have been made to exploit the differing coordination abilities of the β-diketonates and their thio analogues in separation chemistry. In part, this may result from the relative aqueous instability of the thioketonate ligands in the presence of many metal ions.

In previous reports from our laboratory[7-12] we have described some fascinating coordination characteristics of a family of bifunctional (carbamoylmethyl)phosphonates (CMP), $(RO)_2P(O)CH_2C(O)NEt_2$, and (carbamoylmethyl)phosphine oxides (CMPO), $R_2P(O)CH_2C(O)NEt_2$. Initially, these ligands appear to be closely related to β-diketones; however, they differ in some important ways. Most notably, the CMP and CMPO ligands are much weaker acids and consequently they normally bind as neutral ligands.[12] Furthermore, Horwitz and co-workers[13] have characterized the liquid-liquid extraction properties of selected CMP and CMPO ligands and found that they extract hard metal ions from strongly acidic aqueous solutions.

As part of our efforts to design new organophosphorus reagents for metal ion separations, we have explored base strength variations in bifunctional (carbamoylmethyl)phosphonates by changes in phosphorus substituents and central methylene group substituents.[7-12] In this report, we describe the synthesis of (carbamoylmethyl)thiophosphonates, $(RO)_2P(S)CH_2C(O)NEt_2$ (R = Et, Bu), and some selected coordination chemistry with several hard metal ions that are often present in nuclear process solutions.

Experimental Section

General Information. Organophosphorus reagents, PCl_3, and NaH were purchased from Aldrich Chemical Co., *N,N*-diethylchloroacetamide was obtained from Fairfield Chemical Co., H_2S was purchased from Matheson Gas Products, and MoO_2Cl_2 was purchased from Alfa Products (Ventron). Infrared spectra were recorded on a Nicolet 6000 FT-IR spectrometer, and NMR spectra were recorded on Varian FT-80A and GE NT-360 spectrometers. The samples were dissolved in deuteriated lock solvent and contained in 5-mm NMR tubes. Spectral standards were 85% H_3PO_4 (^{31}P) and Me_4Si (^1H, ^{13}C).

Preparation of $(RO)_2P(S)CH_2C(O)NEt_2$ (R = Et, Bu). The respective starting materials $(RO)_2PCl$[14] and $(RO)_2P(S)H$[15] were prepared as described in the literature. The remainder of the synthesis is described for R = Et. Diethyl thiophosphonate (0.1 mol, 15.4 g) was added to a pressure-equalized dropping funnel under a dry-nitrogen atmosphere, and the funnel was connected to a previously nitrogen purged 200-mL Schlenk vessel containing 0.12 mol (2.9 g) of NaH and 80 mL of dry THF.[16] The THF solution was cooled to 5 °C with an ice bath, and the

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diethyl thiophosphonate was added slowly over 1 h to the stirred THF solution. The hydrogen evolved from the reaction was swept from the vessel by a slow stream of nitrogen and vented through a mercury bubbler. The mixture was stirred and allowed to warm slowly to 25 °C over 8 h. The resulting light yellow solution was filtered through a fine-pore fritted funnel under dry nitrogen and the filtrate transferred to a 250-mL round-bottom Schlenk vessel. The solution was cooled to −5 °C with an ice–salt bath, and freshly distilled *N,N*-diethylchloroacetamide contained in a dropping funnel (0.1 mol, 14.9 g) was added under nitrogen to the stirred THF solution over 1 h. The mixture was then stirred for 6 h at 25 °C. Suspended NaCl was centrifuged, and the solution containing the product was decanted from the solid. THF was vacuum-evaporated, leaving a yellow oil that was purified by vacuum distillation, producing a colorless oil: bp 85–100 °C (0.1 Torr); yield 14.7 g (55%). The oil is soluble in ethanol, benzene, hexane, $CHCl_3$, Et_2O, and H_2O. Anal. Calcd for $SPO_3NC_{10}H_{22}$: C, 44.98; H, 8.23; N, 5.24. Found: C, 45.92; H, 8.62; N, 5.22. Mass spectrum (*m*/*e* (fragment), relative intensity): 267 (M^+), 13; 239 ($M - C_2H_5^+$), 6; 222 ($M - OC_2H_5^+$), 3; 195 ($M - NC_4H_{10}^+$), 5; 167 ($M - ONC_5H_{10}^+$), 2; 153 ($M - ONC_6H_{12}^+$), 7; 114 ($ONC_6H_{12}^+$), 12; 100 ($ONC_5H_{10}^+$); 72 ($NC_4H_{10}^+$), 100; 44 ($OC_2H_5^+$), 20; 43 (NC_2H_5), 7; 42 (OC_2H_2), 14. Infrared spectrum (thin film, cm^{-1}): 2987 (m), 2976 (m), ν_{CO} 1644 (s), 1459 (m), 1432 (m), 1050 (m), 1025 (s), 960 (m), ν_{PS} 773 (m). NMR spectra (25 °C): $^{31}P\{^1H\}$ (neat) δ 87.9; $^{13}C\{^1H\}$ (C_6D_6) δ 163.2 (J_{PC} = 4.6 Hz, *C*(O)), 62.9 (J_{PC} = 6.2 Hz, *C*H$_2$O), 43.2 (*C*H$_2$N), 41.4 (J_{PC} = 104.3 Hz, P(O)*C*H$_2$C(O)), 40.3 (*C*H$_2$N), 16.2 (J_{PC} = 7.3 Hz, *C*H$_3$CH$_2$O), 14.5 (*C*H$_3$CH$_2$N), 13.0 (CH$_3$*C*H$_2$N); ^1H (C_6D_6) δ 4.25 (C*H*$_2$O), 3.36 (J_{HH} = 7.0 Hz, C*H*$_2$N), 3.31 (J_{PH} = 19.3 Hz, P(S)C*H*$_2$C(O)), 3.29 (J_{HH} = 7.0 Hz, C*H*$_2$N), 1.29 (J_{HH} = 7.1 Hz, C*H*$_3$CH$_2$O), 1.14 (J_{HH} = 7.1 Hz, NCH$_2$C*H*$_3$), 1.01 (J_{HH} = 7.1 Hz, NCH$_2$C*H*$_3$).

The butyl ligand (R = Bu) was prepared in an identical manner. The product was vacuum-distilled: bp 110–140 °C (0.02 Torr); yield 22.7 g (70%). The oil is soluble in hexane, benzene, THF, acetone, $CHCl_3$, and CH_2Cl_2. Anal. Calcd for $SPO_3NC_{14}H_{30}$: C, 52.00; H, 9.35; N, 4.33. Found: C, 52.43; H, 9.32; N, 4.37. Mass spectrum (*m*/*e* (fragment), relative intensity): 324 ($M + H^+$), 7; 267 ($M - C_4H_8^+$), 4: 250 ($M - OC_4H_9^+$), 3; 212 ($M - C_8H_{15}^+$), 33; 194 ($M - OC_8H_{17}^+$), 10; 178 ($M - O_2C_8H_{17}^+$), 10; 139 ($M - NC_{12}H_{26}^+$), 8; 115 ($ONC_6H_{13}^+$), 20; 100 ($ONC_5H_{10}^+$), 18; 74 ($OC_4H_{10}^+$), 21; 72 ($NC_4H_{10}^+$), 100; 57 ($C_4H_9^+$), 28; 44 ($C_3H_8^+$), 35; 42 ($OC_2H_2^+$), 25. Infrared spectrum (thin film, cm^{-1}): 2962 (s), 2935 (m), ν_{CO} 1645 (s), 1462 (m), 1433 (m), 1064 (m), 1023 (s), 977 (s), ν_{PS} 781 (m). NMR spectra (25 °C): $^{31}P\{^1H\}$ (neat) 88.1; $^{13}C\{^1H\}$ (C_6D_6) δ 163.2 (J_{PC} = 4.6 Hz, *C*(O)), 66.6 (J_{PC} = 6.8 Hz, *C*H$_2$O), 41.6 (J_{PC} = 104.0 Hz, P(O)*C*H$_2$C(O)), 32.6 (J_{PC} = 7.0 Hz, *C*H$_2$CH$_2$O), 32.6 (N*C*H$_2$), 32.5 (N*C*H$_2$), 19.0 (*C*H$_2$(CH$_2$)$_2$O), 14.4 (NCH$_2$*C*H$_3$), 13.7 (*C*H$_3$(CH$_2$)$_3$O), 13.0 (NCH$_2$*C*H$_3$); ^1H (C_6D_6) δ 3.90 (OC*H*$_2$), 3.13 (J_{HH} = 6.9 Hz, NC*H*$_2$), 3.03 (J_{PH} = 19.5 Hz, P(O)C*H*$_2$C(O)), 1.44 (C*H*$_2$CH$_2$O), 1.21 (C*H*$_2$(CH$_2$)$_2$O), 0.90 (NCH$_2$C*H*$_3$), 0.85 (NCH$_2$C*H*$_3$), 0.73 (J_{HH} = 7.5 Hz, C*H*$_3$(CH$_2$)$_3$O).

Preparation of Coordination Complexes. The hydrated nitrate salts $La(NO_3)_3$, $Nd(NO_3)_3$, $Er(NO_3)_3$, and $UO_2(NO_3)_2$ (2 mmol) were dissolved in 10 mL of 95% ethanol, and 5 mL of an ethanol solution of $(EtO)_2P(S)CH_2C(O)NEt_2$ (2–4 mmol) was added to each with stirring. The solutions were evaporated to dryness, leaving sticky oils or a glassy solid (UO_2^{2+} complex). The residues were washed with diethyl ether (2 x 10 mL) and characterized. Only in the case of the uranyl salt was a stable complex isolated that contained thiophosphonate ligand. Anal. Calcd for $US_2P_2O_{14}N_4C_{20}H_{44}$: C, 25.87; H, 4.78; N, 6.03. Found: C, 22.7; H, 4.4; N, 4.7. Infrared spectrum (film, cm^{-1}): 2984 (m), ν_{CO} 1588 (s), 1525 (s), 1487 (m), 1283 (m), 1021 (s), 936 (w), 829 (w), ν_{PS} 775 (w); 747 (w). NMR spectrum: $^{31}P\{^1H\}$ δ 87.6.

Preparation of Complex (3). The complex $MoO_2Cl_2[(C_2H_5O)_2P(O)CH_2C(O)N(C_2H_5)_2]_2$ was prepared by addition of 1.3 mmol of MoO_2Cl_2 dissolved in 15 mL of a 50/50 (v/v) mixture of Et_2O and ethanol to 20 mL of ethanol containing 2.9 mmol of $(EtO)_2P(S)CH_2C(O)NEt_2$. The solution was stirred for 1 h, and then the solvents were allowed to evaporate. The resulting blue solid was washed with Et_2O (2 × 5 mL). The complex was then dissolved in 20 mL of ethanol and the solvent allowed to evaporate slowly overnight. The resulting product was a blue oil, which slowly deposited blue crystals suitable for single-crystal X-ray diffraction analysis. Anal. Calcd for $MoCl_2S_2P_2O_8N_2C_{20}H_{44}$: C, 32.75; H, 6.05. Found: C, 32.72; H, 6.39. Infrared spectrum (KBr pellet, cm^{-1}): 2985 (m), 1597 (s), ν_{CO} 1581 (s), 1477 (m), 1458 (m), 1446 (s), 1050 (s), 1020 (s), 966 (m), 900 (m), ν_{PS} 765 (m). NMR spectra: $^{31}P\{^1H\}$ (C_6D_6) δ 86.8; $^{13}C\{^1H\}$ (C_6D_6) δ 163.2 *C*(O), 62.6 (J_{PC} = 6.1 Hz, PO*C*H$_2$); 42.8 (J_{PC} = 100.9 Hz, P(O)*C*H$_2$C(O)), 42.7 (N*C*H$_2$), 40.1 (N*C*H$_2$), 15.7 (J_{PC} = 7.0 Hz, POCH$_2$*C*H$_3$), 13.9 (NCH$_2$*C*H$_3$), 12.5 (NCH$_2$*C*H$_3$).

Table I. Experimental Data for the X-ray Diffraction Study of $MoO_2Cl_2[(C_2H_5O)_2P(S)CH_2C(O)N(C_2H_5)_2]_2$

(A) Crystal Parameters at −38 °C

cryst syst: monoclinic	mol wt = 733.55
space group: *C*2/*c* (No. 15)	V = 3383.5 (9) Å^3
a = 12.473 (4) Å	ρ_{calcd} = 1.44 g cm^{-3}
b = 15.191 (7) Å	μ = 7.88 cm^{-1}
c = 17.951 (6) Å	F(000) = 1520
β = 95.87 (3)°	
Z = 4	

(B) Data Collection

diffractometer: Syntex P3/F
radiation: Mo Kα ($\bar{\lambda}$ = 0.71069 Å)
monochromator: highly oriented graphite cryst
reflcns measd: $+h,+k,\pm l$
2θ range: 1–55°
scan type: Ω
scan speed: 6–30° min^{-1}
scan range: $(\omega_0 - 1.1)-(\omega_0 + 1.25)°$
pkgd measmts: stationary cryst and counter; at the beginning and end of Ω scan, each for one-fourth of the total Ω scan time
std reflcns: 3 measd every 141 reflcns (400; 040; 004); no signif changes in intens obsd
total reflcns collected: 8993
unique reflcns collected: 3887
obsd reflcns used in refinement: 2670 with $F \geq 5\sigma(F)$
weighting scheme: $1/[\sigma(F)^2 + |g|(F^2]$, g = 0.00303
no. of params refined: n = 168
$R = \sum||F_o| - |F_o||/\sum|F_o| = 5.6\%$
$R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 5.9\%$
GOF $= [\sum(|F_o| - |F_c|)^2/(m - n)]^{1/2} = 0.97$

Crystal Structure Determination. A single crystal (0.18 mm × 0.18 mm × 0.30 mm) was placed in a glass capillary, and the crystal was centered on a Syntex P3/F automated diffractometer. Determinations of the crystal class, orientation matrix, and unit cell dimensions were performed in a standard manner.[8] Data were collected at −38 °C in the ω-scan mode by using Mo Kα radiation, a scintillation counter, and pulse height analyzer. The data collection parameters are summarized in Table I. Collected data were consistent with the monoclinic space group *C*2/*c*. Corrections for absorption were made empirically on the basis of ψ scans: R before correction, 2.8%; R after correction, 1.7%. The maximum and minimum transmission factors were 0.61 and 0.53, respectively. Redundant and equivalent data were averaged and converted to unscaled $|F_o|$ values after corrections for Lorentz and polarization effects.

Solution and Refinement of the Structure. Calculations were performed with the R3/SHELXTL structure determination package.[17] Neutral-atom scattering factors used were those resident in the programs.[17] Least-squares refinement in this package uses a blocked-cascade algorithm with full-matrix blocks of 103 parameters.[18] Anomalous dispersion terms were included for atoms with $Z > 2$. The solution and refinement of the structure were based on 2670 reflections with $F \geq 5\sigma(F)$. The structure was solved by interpretation of the Patterson map on trial positions for Mo, P, and Cl. Phasing on these atoms provided positions for the remaining heavy atoms. Isotropic blocked least-squares refinements on the non-hydrogen atoms converged with R = 12%. Application of individual anisotropic thermal parameters to all non-hydrogen atoms resulted in R_F = 6.9%. Neutral-atom scattering factors were used and the hydrogen atoms included in idealized positions, fixed at 0.96 Å from the parent atom and riding on the position of the parent atom. Least-squares refinements including the hydrogen atoms gave R_F = 5.6% and R_{wF} = 5.9% on 168 parameters and 2670 reflections. A final difference map showed the highest peak to be 2.0 e Å^{-3} 1.06 Å from the Mo atom and 1.34 Å from Cl. This is midway between the Mo–Cl bond and is probably due to a series of termination effects and errors in the data. The troughs in the difference map amounted to −1.39 e Å^{-3}. The second

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(16) Abbreviations used in the text include the following: THF = tetrahydrofuran; Et = ethyl; Bu = butyl; Ph = phenyl; DMF = dimethylformamide.

(17) Sheldrick, G. M. *Nicolet SHELXTL Operations Manual*; Nicolet XRD Corp.: Cupertino, CA, 1981. SHELXTL uses absorption, anomalous dispersion, and neutral atom scattering factor data compiled in: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 55–60, 99–101, 149–150. Absorption corrections (ψ scans) were accomplished with the program resident in the SHELXTL package.

(18) A general description of the least-squares algebra is found in: Ahmed, F. R.; Hall, S. R.; Huber, C. P., Eds. *Crystallographic Computing*; Munksgaard: Copenhagen, 1970; p 187. The least-squares refinement minimizes $\sum w(|F_o| - |F_c|^2)$, where $w = 1/[\sigma(F)^2 + gF^2]$.

Table II. Fractional Coordinates and Their Esd's for $MoO_2Cl_2[(C_2H_5O)_2P(S)CH_2C(O)N(C_2H_2)_2]_2$

atom	*x/a*	*y/b*	*z/c*
Mo	0.00000	0.11863 (4)	0.25000
Cl	0.11949 (11)	0.09325 (10)	0.35906 (7)
S	0.40181 (13)	0.13853 (11)	0.07940 (10)
P	0.29536 (10)	0.05462 (8)	0.10347 (7)
O(1)	0.0923 (2)	0.0045 (2)	0.2109 (2)
O(2)	0.3231 (3)	−0.0458 (2)	0.0960 (2)
O(3)	0.1819 (3)	0.0602 (2)	0.0554 (2)
O(4)	0.0800 (3)	0.1893 (2)	0.2073 (2)
N	0.2292 (3)	−0.0844 (3)	0.2525 (2)
C(1)	0.2705 (4)	0.0595 (3)	0.2008 (3)
C(2)	0.1924 (3)	−0.0098 (3)	0.2230 (2)
C(3)	0.1540 (4)	−0.1537 (3)	0.2725 (3)
C(4)	0.1354 (5)	−0.2208 (4)	0.2096 (3)
C(5)	0.3455 (4)	−0.1042 (4)	0.2697 (3)
C(6)	0.3862 (5)	−0.0737 (7)	0.3489 (4)
C(7)	0.3460 (5)	−0.0837 (5)	0.0243 (3)
C(8)	0.3621 (7)	−0.1790 (5)	0.0337 (5)
C(9)	0.1353 (5)	0.1414 (4)	0.0248 (3)
C(10)	0.0431 (6)	0.1198 (4)	−0.0293 (3)

highest peak in the difference map amounted to -1.39 e Å^{-3}. The second highest peak in the difference map was 0.96 e Å^{-3} 0.77 Å from O(4). This peak is much smaller in amplitude than the trough, and because of this no significance was attached to the peak. The observed and calculated structure factor amplitudes, hydrogen atom positions, and anisotropic thermal parameters are available in the supplementary material. The non-hydrogen atom positional parameters are listed in Table II.

Results and Discussion

Although methylenediphosphine sulfides, $R_2P(S)CH_2P(S)R_2$, monothio β-diketones, $RC(S)CH_2C(O)R'$, and dithio β-diketones, $RC(S)CH_2C(S)R'$, are well-known ligands, the mixed bifunctional ligands $(RO)_2P(S)CH_2C(O)R'$ and $(RO)_2P(O)CH_2C(S)R'$ have not been reported. Two representatives of the former class, $(RO)_2P(S)CH_2C(O)NEt_2$ (R = Et, Bu), have been prepared in good yield and high purity in this study, and the synthesis is summarized in eq 1–4.

$$2(RO)_3P + PCl_3 \xrightarrow[Et_2O]{\Delta} 3(RO)_2PCl \tag{1}$$

$$(RO)_2PCl + H_2S \xrightarrow[Et_2O]{0\ ^\circ C} (RO)_2P(S)H + HCl \tag{2}$$

$$(RO)_2P(S)H + NaH \xrightarrow[5\ ^\circ C]{THF} Na^+[(RO)_2P(S)^-] + H_2 \tag{3}$$

$$Na^+[(RO)_2P(S)^-] + ClCH_2C(O)NEt_2 \xrightarrow[-5\ ^\circ C]{THF} (RO)_2P(S)CH_2C(O)NEt_2 + NaCl \quad R = Et\ (\mathbf{1}),\ Bu\ (\mathbf{2}) \tag{4}$$

$$2\ \mathbf{1} + UO_2(NO_3)_2 \xrightarrow[Et_2O]{EtOH} UO_2(NO_3)_2[(EtO)_2P(S)CH_2C(O)NEt_2]_2 \tag{5}$$

$$2\ \mathbf{1} + MoO_2Cl_2 \xrightarrow[Et_2O]{EtOH} \underset{\mathbf{3}}{MoO_2Cl_2[(EtO)_2P(S)CH_2C(O)NEt_2]_2} \tag{6}$$

The ligands have been characterized by elemental analyses and mass, infrared, and NMR spectroscopy. In particular, the infrared spectra for **1** and **2** have been partially assigned and the absorptions can be compared with characteristic bands for bifunctional CMP ligands and monofunctional phosphoryl, thiophosphoryl, and carbamide compounds. The ν_{CO} bands in **1** and **2** appear at 1644 and 1645 cm^{-1}, respectively, and these are similar to ν_{CO} = 1651 and 1648 cm^{-1} in the CMP ligands $(EtO)_2P(O)CH_2C(O)NEt_2$[8] and $(i\text{-}PrO)_2P(O)CH_2C(O)NEt_2$[7] and ν_{CO} = 1647 cm^{-1} for *N*,*N*-diethylacetamide.[19] Bands for **1** and **2** at 773 and 781 cm^{-1} are assigned to ν_{PS} on the basis of vibrations[20] in other thiophosphoryl compounds in the range 862–515 cm^{-1}. The intensities of ν_{PS} in **1** and **2** are noticeably less than intensities for ν_{PO} found in CMP ligands.[20] On the other hand, the coupled ν_{POC} stretching frequencies in **1** and **2**, 1064–1023 cm^{-1}, are more intense than the corresponding bands in the CMP ligands.

The ^1H, ^{13}C, and ^{31}P NMR data have been completely assigned, and several features merit discussion. The ^{31}P resonances for **1** and **2** appear as singlets at δ 87.9 and 88.1, and these resonances compare well with the resonances found for $(MeO)_2(CH_3)PS$, δ 80.5, and for $(EtO)_2(CH_3)PS$, δ 94.9.[21] The $^{13}C\{^1H\}$ NMR spectra are similar to the spectra for the related CMP ligands $(EtO)_2P(O)CH_2C(O)NEt_2$ (DEDECMP) and $(BuO)_2P(O)CH_2C(O)NEt_2$ (DBDECMP). Low-field resonances for **1** and **2**, δ 163.2 (J_{PC} = 4.6 Hz), can be assigned to the carbonyl carbon atom. These data are similar to the carbonyl resonances for DEDECMP, δ 164.3 (J_{PC} = 5.3 Hz), and DBDECMP, δ 164.2 (J_{PC} = 5.2 Hz).[22] The $P(S)\mathit{C}H_2C(O)$ methylene carbon resonances for **1**, δ 41.4 (J_{PC} = 104.3 Hz), and **2**, δ 41.6 (J_{PC} = 104.0 Hz), can be compared with the $P(O)\mathit{C}H_2C(O)$ resonances in DEDECMP, δ 34.1 (J_{PC} = 132.3 Hz), and DBDECMP, δ 34.0 (J_{PC} = 131.6 Hz). The decrease in the P—C coupling constant with thio substitution is consistent with Bent's rule,[23] which would predict greater s character in a P=S bond relative to a P—O bond and subsequently greater p character in a $P—CH_2$ bond in the thiophosphonate and a smaller J_{PC} value. Resonances for the syn and anti conformers of the methyl and methylene carbon atoms of the amide group are resolved, which indicates that there is hindered rotation about the $(O)C—NEt_2$ bond. A similar effect is seen in DEDECMP and DBDECMP.[22]

The ^1H NMR data for **1** and **2** also compare favorably with related resonances in DEDECMP and DBDECMP. Separate resonances for the syn and anti protons in the methylene and methyl hydrogens of the amide ethyl groups are resolved. Lastly, the protons on the $P(S)C\mathit{H}_2C(O)$ methylene group appear at δ 3.31 (J_{PH} = 19.3 Hz) and 3.03 (J_{PH} = 19.5 Hz) in **1** and **2**, respectively. These resonances are slightly downfield of the resonances in DEDECMP, δ 2.92 (J_{PH} = 21.9 Hz), and in DBDECMP, δ 2.86 (J_{PH} = 22.0 Hz). The positions of the methylene resonances in these phosphonate and thiophosphonate ligands suggest that they exist in the keto form. β-Diketones and β-thioketones, on the other hand, have been found to display central methine proton resonances in the region δ 5.0–6.5, which have been interpreted to indicate a predominance of the enol form of these ligands.[5] There are no resonances in this region for **1** or **2**.

On the basis of the known coordination chemistry for β-diketones, monothio β-diketones and CMP ligands, it is expected that the (carbamoylmethyl)thiophosphonates will be weak proton donors and consequently the coordination chemistry should be dominated by the neutral keto form of the ligand. In addition, it is expected that the strongest complexes will be formed with softer metal ions. In order to partially test this expectation, the coordination chemistry of **1** with the relatively hard metal salts $La(NO_3)_3$, $Nd(NO_3)_3$, $Er(NO_3)_3$, $UO_2(NO_3)_2$, and MoO_2Cl_2 was initially surveyed. Extraction coordination chemistry with potentially softer later actinide(III) ions is being examined in separate studies at Los Alamos National Laboratory.

Combinations of **1** with lanthanide nitrates results in the formation of very weak adducts,[24] and the ligand can be back-ex-

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(19) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. Spectrometric Identification of Organic Compounds, 4th ed.; Wiley: New York, 1981; p 124.

(20) Emsley, J.; Hall, D. *The Chemistry of Phosphorus*; Harper and Row: London, 1976; pp 92–98. Corbridge, D. E. C. *The Structural Chemistry of Phosphorus*; Elsevier: Amsterdam, 1974. The lower intensity observed for ν_{PS} compared to that for ν_{PO} has been attributed to the smaller polarity of the P=S bond.

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(24) Preliminary liquid–liquid extraction measurements for Eu(III) and Y(III) in aqueous nitric acid solutions against diisopropylbenzene solutions of **2** show very small partition coefficients: 10^{-3}–10^{-4}. Blaha, S. Ph.D. Thesis, University of New Mexico, 1986.

Table III. Selected Bond Distances (Å) and Angles (deg) for $MoO_2Cl_2[(C_2H_5O)_2P(S)CH_2C(O)N(C_2H_5)_2]_2$

	(A) Bond Distances		
Mo–Cl	2.368 (1)	Mo–O(1)	2.234 (3)
Mo–O(4)	1.702 (4)	P–S	1.921 (2)
P–O(2)	1.572 (4)	P–O(3)	1.583 (4)
N–C(2)	1.312 (6)	P–C(1)	1.807 (5)
C(2)–O(1)	1.265 (5)	C(1)–C(2)	1.515 (6)
	(B) Bond Angles		
Cl–Mo–Cl′	161.3 (1)	O(1)–Mo–O(1′)	101.7 (3)
O(4)–Mo–O(4′)	78.1 (2)	C(2)–O(1)–Mo	127.6 (3)
O(1)–Mo–O(4)	90.2 (2)	O(1)–Mo–Cl	80.4 (1)
O(4)–Mo–Cl	97.3 (1)	S–P–O(2)	117.5 (2)
S–P–O(3)	116.2 (2)	O(2)–P–O(3)	101.4 (2)
S–P–C(1)	112.4 (2)	P–C(1)–C(2)	113.9 (3)
O(1)–C(2)–N	121.0 (4)	O(1)–C(2)–C(1)	119.0 (4)
N–C(2)C(1)	119.9 (4)		

tracted from the metal by several ether washings. Adduct formation in solution is indicated by shifts in the carbonyl stretching frequency compared to that the free ligand: $\Delta\nu_{CO}$ = 46, 46, and 39 cm^{-1} for La, Nd, and Er, respectively. Small shifts in the thiophosphoryl stretching frequency in these adducts are also seen: $\Delta\nu_{PS}$ = 9, 14, and 21 cm^{-1}. The latter shifts may result from solvent interactions with the thiophosphoryl group, although weak lanthanide–thiophosphoryl interactions cannot be ruled out. The complex with uranyl nitrate is more stable, yet it has proven difficult to purify and good elemental analyses have not been obtained. The results suggest that a bis complex, $UO_2(NO_3)_2(\mathbf{1})_2$, is formed as shown in eq 5. Infrared spectral shifts, $\Delta\nu_{CO}$ = 56 cm^{-1} and $\Delta\nu_{PS}$ = 1 cm^{-1}, suggest that the ligands are bonded to the uranyl ion through the carbonyl oxygen atoms only. The ν_{CO} coordination shift, in fact, is considerably larger than the shift recorded for a the stable CMP–uranyl complex. $UO_2(NO_3)$-$[(i\text{-}PrO)_2P(O)CH_2C(O)NEt_2]$, $\Delta\nu_{CO}$ = 36 cm^{-1}, in which the single CMP ligand is bonded in a bidentate manner to the uranyl group.

A dark blue oil (**3**) results from the 1:2 combination of MoO_2Cl_2 and the ligand **1** in ethanol, and small blue crystals deposit slowly from the oil. Partial elemental analyses are consistent with the formation of a 1:2 metal:ligand complex as described in eq 6. An infrared spectrum of **3** obtained from a KBr pellet shows two strong absorptions at 1597 and 1581 cm^{-1}, which can be assigned to the carbonyl stretching frequencies, ν_{CO}.[25] The down-frequency coordination shifts relative to those of **1** are 47 and 63 cm^{-1}, and these are comparable to the shift found in $MoO_2Cl_2[(i\text{-}PrO)_2P(O)CH_2C(O)NEt_2]$ (**4**), $\Delta\nu_{CO}$ = 52 cm^{-1}, in which the single CMP ligand is bonded in the solid state to the molybdenyl group in a bidentate fashion.[26] The infrared spectrum for **3** also shows an absorption ν at 765 cm^{-1}, which is shifted only slightly from the corresponding band in the free ligand. The small shift indicates no significant interaction between the molybdenyl unit and the sulfur atom. This is opposite to the trend found in **4**, where $\Delta\nu_{PO}$ = 60, 85 cm^{-1}. The dioxomolybdenum terminal symmetric and asymmetric stretches in **3** are assigned at 966 and 900 cm^{-1}, and these absorptions can be compared with those in **4**: 950 and 909 cm^{-1}.[26]

The $^{31}P\{^1H\}$ NMR spectrum for **3** shows a single resonance at δ 86.8 slightly upfield of the resonance in **1**, δ 87.9. A small downfield shift, δ = 1.3, is seen for **4**. The $^{13}C\{^1H\}$ spectrum does not vary significantly from the spectrum of **1**. In particular, there is no shift in the resonance for the coordinated carbonyl groups in **3** compared to those for **1**. A similar effect was seen with the formation of **4**.

A single-crystal X-ray diffraction analysis of **3** was undertaken in order to unambiguously determine the stoichiometry and structure. The structure contains discrete monomeric units of formula $MoO_2Cl_2[(EtO)_2P(S)CH_2C(O)NEt_2]_2$ with four molecules per unit cell. A view of the molecule is shown in Figure 1, and selected bond distances and angles are summarized in Table III.

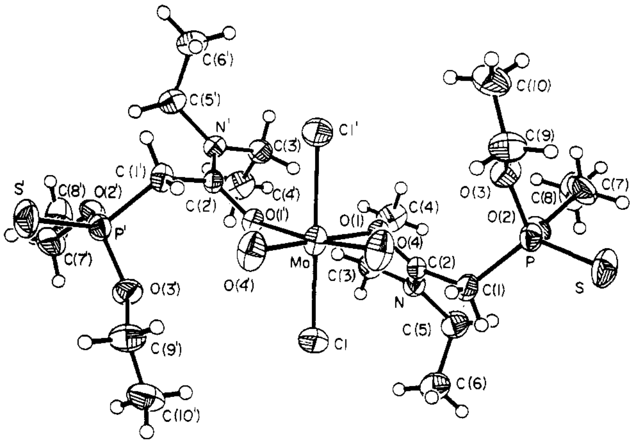

Figure 1. Molecular geometry and atom-labeling scheme for $MoO_2Cl_2[(C_2H_5O)_2P(S)CH_2C(O)N(C_2H_5)_2]_2$ (50% probability ellipsoids). Primed atoms are related to unprimed atoms by the symmetry operation $x, y, z \rightarrow -x, y, 0.5 - z$.

The molecule possesses a crystallographic twofold rotation axis, which relates one half of the molecule to the other half. The inner coordination sphere consists of two equivalent chlorine atoms, two equivalent molybdenyl oxygen atoms, and two equivalent ligand carbonyl oxygen atoms, which are arranged in a distorted octahedron. The chlorine atoms are trans to one another, and they make an angle Cl–Mo–Cl′ of 161.3 (1)°. The molybdenyl oxygen atoms are cis, and they make an O(4)–Mo–O(4′) angle of 78.1 (2)°, while the carbonyl oxygen atoms are cis to one another, making an angle O(1)–Mo–O(1′) = 101.7 (3)°. Similar coordination geometries are found in $MoO_2Cl_2[(i\text{-}PrO)_2P(O)CH_2C(O)NEt_2]$,[26] $MoO_2Cl_2(Ph_3PO)_2$,[27] and $MoO_2Cl_2(DMF)_2$.[28]

The Mo–Cl bond distance, 2.368 (1) Å, is slightly shorter than the corresponding distances in $MoO_2Cl_2[(i\text{-}PrO)_2P(O)CH_2C(O)NEt_2]$ (**4**), 2.376 (1) and 2.384 (1) Å, and $MoO_2Cl_2(Ph_3PO)_2$, 2.397 (1) and 2.388 (1) Å, but slightly longer than the distance in $MoO_2Cl_2(DMF)_2$, 2.341 (7) Å. The Cl–Mo–Cl bond angles in these complexes, 162.2 (1), 164.62 (5), and 161.3°, respectively, are also comparable to the angle in **3**. The cis molybdenyl bond distance Mo = O(4), 1.702 (4) Å, in **3** is slightly longer than the corresponding distances in **4**, 1.687 (2) and 1.677 (2) Å, in $MoO_2Cl_2(Ph_3PO)_2$, 1.695 (1) and 1.673 (1) Å, and in $MoO_2Cl_2(DMF)$, 1.68 (1) Å. In addition, the O(4)=Mo=O(4′) angle is slightly smaller than the angle in the other three complexes: 102.8 (1), 103.17 (7), and 102.2 (7)°. The carbonyl oxygen atoms of the (carbamoylmethyl)thiophosphonate ligands make a Mo—O(C) bond distance of 2.234 (2) Å, which is slightly shorter than the Mo—O(C) bond distance in the bidentate complex **4**, 2.246 (2) Å. The (C)O—Mo—O′(C′) interligand ("bite") angle in **3** is similar to those found in **4**, 78.9 (1)°, $MoO_2Cl_2(Ph_3PO)_2$, 77.81 (5)°, and $MoO_2Cl_2(DMF)_2$, 76.2 (5)°. The complete picture of angular distortions in **3** is similar to that found in the other complexes and probably results from a combination of strong nonbonded repulsions between cis molybdenyl oxygen atoms and cis oxygen donor ligand atoms.

As may be seen in Figure 1, the thiophosphoryl groups are directed completely away from the central metal core of the complex, and they are not involved in any noticeable way with the coordination chemistry. The P=S bond distance, 1.921 (2) Å, falls within the range of uncoordinated thiophosphoryl distances, 1.85–1.96 Å. The carbonyl distance C(2)–O(1) = 1.265 (5) Å is essentially identical with the coordinated carbonyl distance in **4**, 1.262 (3) Å. The remaining bond distances and angles in the

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(25) Two carbonyl stretching frequencies ($a_1 + b_2$) would be predicted for a cis–trans–cis molybdenyl complex $MoO_2Cl_2(O{=}CR)_2$ with idealized C_{2v} symmetry.

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(carbamoylmethyl)thiophosphonate fragment are similar to the distances and angles found in metal-coordinated CMP ligands.

The chemical and structural data presented here indicate that bifunctional (carbamoylmethyl)thiophosphonate ligands interact only weakly through their carbonyl base site with relatively hard metal centers that are important constituents in nuclear process solutions. Two important questions related to the coordination ability of these ligands remain to be addressed: How successfully will the neutral ligands complex softer metal centers present in nuclear process solutions, and can an anionic form of the ligand, $[(RO)P(S)(O)CH_2C(O)NR'_2{}^-]$, be prepared and will it provide improved coordination ability with hard metal ions? On the basis of studies of Pinkerton and co-workers,[29] it might be expected that an anionic thiophosphonate would serve as an improved extractant for lanthanide ions. Forthcoming communications from our laboratory will address these points.

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Registry No. 1, 108675-65-6; 2, 108675-66-7; 3, 108675-68-9; $UO_2(NO_3)_2(1)_2$, 108675-67-8; $(EtO)_2P(S)H$, 999-01-9; $(BuO)_2P(S)H$, 17529-47-4; La, 7439-91-0; Nd, 7440-00-8; Er, 7440-52-0; *N,N*-diethylchloroacetamide, 2315-36-8.

Supplementary Material Available: Tables SI–SIV, listing hydrogen atom positional parameters, thermal parameters, and bond distances and bond angles (4 pages); Table SV, listing calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

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[29] Pinkerton, A. A. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 495. Pinkerton, A. A.; Schwarzenback, D. *J. Chem. Soc., Dalton Trans.* **1976**, 2466.

Contribution from the Department of Chemistry,
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Synthesis of Polyfluoroalkyl Esters of (Fluorosulfonyl)difluoroacetic Acid and Diesters of Sulfonyldifluoroacetic Acid

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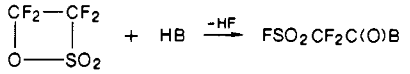
Several new polyfluoroalkyl(fluorosulfonyl)difluoroacetates, $R_fOC(O)CF_2SO_2F$ ($R_f = CF_3CH_2$, $CF_3CF_2CH_2$, $CF_3CF_2CF_2CH_2$, $(CF_3)_2C(CH_3)$, $CF_3CH(CH_3)$, $(CF_3)_2CH$, $C_7F_{15}CH_2$, $CH_2(CF_2)_3CH_2OC(O)CF_2SO_2F$), diesters of sulfonyldifluoroacetic acid, $R_fOC(O)CF_2SO_2OR_f'$ ($R_f = CF_3CH_2$, $(CF_3)_2CH$; $R_f' = CF_3CH_2$, $(CF_3)_2CH$), and alkyl (fluorosulfonyl)difluoroacetates, $RCH_n(CH_2OC(O)CF_2SO_2F)_{3-n}$ ($R = CH_3$, $n = 0$; $R = O_2N$, $n = 0$; $R = OC(O)CF_2SO_2F$, $n = 2$; $R = CH_2OC(O)CF_2SO_2F$, $n = 0$), resulted from the reaction of tetrafluoroethane-β-sultone with polyfluoroalkyl alcohols or polyfluoroalkoxides and alkanediols, -triols, and a -tetraol.

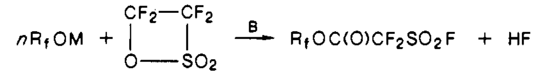
Introduction

Previous investigations dealing with the reactions of tetrafluoroethane-β-sultone with various nucleophilic reagents, such as amines, mercaptans, alcohols, hydrogen sulfide, and carboxylic acids gave rise to the corresponding derivatives of (fluorosulfonyl)difluoroacetic acid.[1,2]

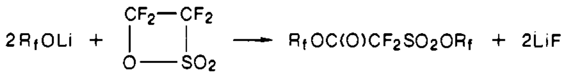


B = e.g., C_6H_5S, C_6H_5NH, $C_6H_5(CH_3)N$, CH_3O, i-C_3H_7O, $O(CH_2)_2NCH_2CH_2$, SCN, $(C_6H_5)_2N$, Et_2N

In our continuing efforts toward the syntheses of precursors to new highly conducting, hydrolytically and thermally stable polyfluorinated sulfonic acids, we have taken advantage of the electrophilic sulfur center in sultones to prepare a variety of mono-, di-, tri-, and tetrasulfonyl fluorides. Tetrafluoroethane-β-sultone was reacted with polyfluoroalkyl alcohols to yield new polyfluoroalkyl (fluorosulfonyl)difluoroacetates, and di(polyfluoroalkyl) esters of sulfonyldifluoroacetic acid.

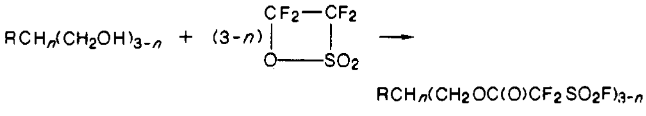


$R_f = CF_3CH_2$, $CF_3CF_2CH_2$, $CF_3CF_2CF_2CH_2$, $C_7F_{15}CH_2$; $M = H$; B = KF, NaF; $n = 1$
$= CF_3(CH_3)CH$, $(CF_3)_2CH$, $(CF_3)_2C(CH_3)$; M = Li; $n = 1$
$= CH_2(CF_2)_3CH_2$; $M = H$; B = KF, NaF; $n = 0.5$



$R_f = CF_3CH_2$, $(CF_3)_2CH$

In addition, alkyl poly[(fluorosulfonyl)difluoroacetates] were synthesized.



$R = CH_3$, $n = 0$; $R = O_2N$, $n = 0$; $R = OC(O)CF_2SO_2F$, $n = 2$; $R = CH_2OC(O)CF_2SO_2F$, $n = 0$

Results and Discussion

Polyfluoroalkyl (fluorosulfonyl)difluoroacetates were synthesized in good yields by the reaction between tetrafluoroethane-β-sultone and polyfluoroalkoxides or polyfluoroalkyl al-

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