heated at 100 °C for days with no apparent reaction. (Eventually there is some change in the IR spectrum, but only amorphous powders could be isolated.) Adding further support to our theory that a coordinated chalcogen ring is an intermediate in the oxidation reaction is our isolation of a selenium ring coordinated to rhenium(I) from[23]

$$Re_2(CO)_{10} + Se_n^{2-} \rightarrow [Re_2(Se_4)_2(CO)_6]^{2-}$$

The facile reaction of coordinated dithiocarbonate with elemental sulfur prompts speculation that it may be an intermediate in the oxidative decarbonylation reaction observed with molybdenum and tungsten as well. Thus, rearrangement of the coordinated polychalcogen could form dichalcogenocarbonate. Rapid reaction of this with elemental chalcogen could lead to the observed products and higher order polychalcogens, which are well-known.[24] This mechanism is illustrated as follows:

$$[(CO)_4ME_4]^{2-} + \tfrac{1}{2}E_4^{2-} \rightarrow [M(E_2CO)_3]^{3-} + CO$$

$$2[M(E_2CO)_3]^{3-} + 2E \rightarrow 2ME_4^{2-} + 6CO + E_6^{2-}$$

However, at no time in the course of the reactions with molybdenum and tungsten carbonyls do we see any IR evidence for the existence of dithio- or diselenocarbonates. This is not to say that they cannot exist as intermediates in low concentration and react quickly with elemental chalcogen in solution to produce the observed metal chalcogenides. But under our experimental conditions, we do not detect this potential intermediate.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corp. for support of this work.

Supplementary Material Available: For the structure of $[(C_6H_5)_4P]_3[Cr(S_2CO)_3]$ complete tables of atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, and positions of hydrogen atoms (8 pages); a table of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131, and Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Synthesis and Coordination Properties of (Sulfinylmethyl)phosphonates and (Sulfonylmethyl)phosphonates. Crystal and Molecular Structure Determinations for $UO_2(NO_3)_2[(i\text{-}C_3H_7O)_2P(O)CH_2S(O)_2C_6H_{11}]_2$ and $Gd(NO_3)_3[(i\text{-}C_3H_7O)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)]\cdot H_2O$

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The bifunctional (sulfonylmethyl)phosphonates $(i\text{-}C_3H_7O)_2P(O)CH_2S(O)_2C_6H_{11}$, $(i\text{-}C_3H_7O)_2P(O)CH_2S(O)_2(p\text{-}CH_3C_6H_4)$, and $(C_6H_5)_2P(O)CH_2S(O)_2N(CH_3)_2$ and (sulfinylmethyl)phosphonate $(i\text{-}C_3H_7O)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)$ have been synthesized. The ligands have been characterized by spectroscopic methods, and selected coordination chemistry with $UO_2(NO_3)_2$, $La(NO_3)_3$, and $Gd(NO_3)_3$ has been evaluated. The structures of two complexes, $UO_2(NO_3)_2[(i\text{-}C_3H_7O)_2P(O)CH_2S(O)_2C_6H_{11}]_2$ (**2**) and $Gd(NO_3)_3[(i\text{-}C_3H_7O)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)]\cdot H_2O$ (**8**), have been determined by single-crystal X-ray diffraction techniques at 23 °C. Complex **2** crystallized in the monoclinic space group $P2_1$ with $a = 8.374$ (4) Å, $b = 25.423$ (3) Å, $c = 10.031$ (2) Å, $\beta = 100.49$ (3)°, $Z = 2$, and $\rho_{calcd} = 1.65$ g cm^{-3}. The molecular structure of **2** has a linear UO_2^{2+} ion bonded at its equator by four oxygen atoms from two bidentate nitrate ions and by the phosphoryl oxygen atoms of two monodentate (sulfonylmethyl)phosphonate ligands: U–O(uranyl)$_{av}$ = 1.763 (8) Å, U–OP(1) = 2.325 (9) Å, and U–OP(2) = 2.489 (9) Å. The molecular complex **8** crystallized in the monoclinic space group $P2_1/a$ with $a = 9.213$ (3) Å, $b = 21.09$ (1) Å, $c = 13.277$ (6) Å, $\beta = 98.35$ (3)°, $Z = 4$, and $\rho_{calcd} = 1.77$ g cm^{-3}. The molecular structure of **8** features a central Gd(III) ion bonded to six oxygen atoms from three bidentate nitrate groups, two oxygen atoms from one bidentate (sulfinylmethyl)phosphonate ligand with Gd–O(P) = 2.319 (4) Å and Gd–O(S) = 2.340 (5) Å, and a water oxygen atom with Gd–OH_2 = 2.378 (5) Å.

Introduction

Among the numerous bifunctional ligands containing C=O and P=O groups, the (carbamoylmethyl)phosphonates (CMP's), $(RO)_2P(O)CH_2C(O)NR'_2$, have been shown to act as unique and useful extractants for lanthanide (Ln) and actinide (An) trivalent ions in aqueous acid solutions.[1] The extraction ability of these ligands is distinctly different from the extraction characteristics of monofunctional organophosphonates and organoamides. This special behavior has led us to examine model coordination chemistry of CMP-like ligands in order to characterize steric and electronic features that influence ligand binding to Ln(III) and UO_2^{2+} ions.[2] These studies, in turn, have stimulated searches for families of new CMP-like ligands that may provide additional fundamental information on crucial coordination processes responsible for selective extractions. In particular, because of the oxophilicity of Ln and An ions, we have generally sought to combine two functional groups X=O and Y=O, known to be active coordination sites in monofunctional extractants, into single extractants. In that regard, monofunctional organophosphonates, $(RO)_2P(O)R'$, and pyridine *N*-oxides are known to extract Ln(III) and UO_2^{2+} ions under certain conditions, and we have recently reported on the formation of phosphinopyridine *N*,*P*-dioxides and on their coordination chemistry with UO_2^{2+} and selected lanthanides.[3,4] Although the coordination chemistry of CMP and

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phosphinopyridine *N,P*-dioxides has parallels, these ligands display liquid–liquid extraction properties that are quite different.[5] Factors that control the similarities and differences continue to be examined in our group.

Pursuing this theme, others have observed that monofunctional sulfoxides, $R_2S(O)$, function as extractants and synergistic additives for hard metal ion separations,[6] and a limited amount of coordination chemistry of sulfoxides with lanthanide and actinide ions has been reported.[7,8] Much less is known about the relevant extraction properties or coordination chemistry of sulfones, $R_2S(O)_2$.[9] It was of interest, therefore, to develop syntheses for bifunctional (sulfinylmethyl)phosphonates, $R_2P(O)CH_2S(O)R'$, and (sulfonylmethyl)phosphonates, $R_2P(O)CH_2S(O)_2R'$, with donor sites in 1,3-positions and to determine if these types of ligands could form coordination complexes with Ln(III) and UO_2^{2+} ions. We report here on the syntheses of several ligands from these classes and on selected coordination chemistry.

Experimental Section

General Information. Cyclohexyl mercaptan, *p*-tolyl mercaptan, triisopropyl phosphite, *n*-butyllithium, chlorodiphenylphosphine, and methanesulfonyl chloride were purchased from Aldrich Chemical Co. Lanthanide and uranyl nitrates were obtained from Strem Chemicals. All the reactions were carried out under N_2 atmosphere with dried organic solvents, unless specified otherwise. Infrared spectra were recorded on a Nicolet Model 6000 FT-IR spectrometer. Mass spectra were obtained on a Finnigan 4600 GC/MS spectrometer using an electron energy of 70 eV, and the data for the ligands are included in the supplementary material. NMR spectra were obtained on a Varian FT-80A spectrometer. Tetramethylsilane (^{1}H and ^{13}C) and 85% phosphoric acid (^{31}P) were used as spectral standards.

Preparations of Ligands. $(i\text{-}C_3H_7O)_2P(O)CH_2S(O)_2C_6H_{11}$ (1).[10] Chloromethyl cyclohexyl sulfide was prepared according to the procedure given by Fancher[11] for halomethyl aryl thioethers. Diisopropyl (cyclohexylthio)methyl) phosphonate was prepared by the procedure reported by Shahak[12] for dimethyl (methylthio)methyl) phosphonate, and that procedure is described here. Chloromethyl cyclohexyl sulfide, 25 g (0.15 mol), and 53.0 g (0.25 mol) of triisopropyl phosphite were mixed and refluxed for $5^1/_2$ h. The mixture was cooled and then distilled under reduced pressure to give diisopropyl (cyclohexylthio)methyl) phosphonate, $(i\text{-}C_3H_7O)_2P(O)CH_2S(C_6H_{11})$ (bp 160 °C (0.1 Torr)). Yield: 40 g, 91%. Infrared (thin film, cm^{-1}): 1253 (s, $\nu_{P=O}$), 986 (s, ν_{P-O-C}). ^{1}H NMR: (CDCl$_3$): δ 4.9–4.0 (m, OC*H*, SC*H*, 3 H), 2.69 (d, SCH_2P, 2 H, $^2J_{PH}$ = 14.1 Hz), 1.8–1.0 (m, CH_3, –CH_2–, 22 H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 70.7 (d, O*C*H, $^2J_{PC}$ = 6.9 Hz), 44.3 (d, SC_1, $^3J_{PC}$ = 4.1 Hz), 32.8 (s, C_2), 25.8 (s, C_3), 24.5 (d, *C*H$_3$, $^3J_{PC}$ = 3.4 Hz), 24.4 (d, S*C*H$_2$P, $^1J_{PC}$ = 151.0 Hz), 24.0 (d, *C*H$_3$, $^3J_{PC}$ = 2.6 Hz), ^{31}P{^{1}H} NMR (neat): δ 22.0.

The procedure used for the oxidation of diisopropyl ((cyclohexylthio)methyl)phosphonate was similar to the method reported by Shahak[12] for diethyl (((*p*-bromophenyl)sulfonyl)methyl)phosphonate. Diisopropyl ((cyclohexylthio)methyl)phosphonate (38 g, 0.13 mol) was dissolved in 500 mL of benzene, and 250 mL of 25% H_2SO_4 was added to this solution. Potassium permanganate was added in 10-g portions with vigorous stirring of the reaction mixture until the violet color persisted for 20 min. The temperature of the reaction mixture was maintained below 40 °C during the entire process. The manganese dioxide precipitate was dissolved by slow addition of sodium bisulfite. The benzene layer was separated, washed successively with 5% $NaHCO_3$ solution (2 × 100 mL) and water (2 × 200 mL), and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, leaving a colorless oil, $(i\text{-}C_3H_7O)_2P(O)CH_2S(O)_2(C_6H_{11})$, which solidified on standing (mp 49 °C). Yield: 64%. Infrared (thin film, cm^{-1}): 1314 (s, $\nu_{S=O\,asym}$), 1259 (s, $\nu_{P=O}$), 1144 (s, $\nu_{S=O\,sym}$), 1010 (s, ν_{P-O-C}). ^{1}H NMR: (CDCl$_3$): δ 5.0–4.6 (m, OC*H*, SC*H*, 3 H), 3.53 (d, SCH_2P, 2 H, $^2J_{PH}$ = 16.8 Hz), 2.5–1.1 (m, CH_3, –CH_2–, 22 H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 72.7 (d, O*C*H, $^2J_{PC}$ = 6.5 Hz), 61.8 (s, SC_1), 48.2 (d, S*C*H$_2$P, $^1J_{PC}$ = 139.6 Hz), 25.0–23.7 (m, *C*H$_3$, –*C*H$_2$–), ^{31}P{^{1}H} NMR (neat): δ 10.8. Anal. Calcd for $C_{13}H_{27}O_5PS$: C, 47.84; H, 8.34. Found: C, 47.44; H, 8.35.

$(i\text{-}C_3H_7O)_2P(O)CH_2S(O)_2(p\text{-}CH_3C_6H_4)$ (3). Diisopropyl ((*p*-tolylsulfonyl)methyl)phosphonate (**3**) was prepared by employing the same procedure described for **1**. Diisopropyl ((*p*-tolylthio)methyl)phosphonate was prepared by treating chloromethyl *p*-tolyl sulfide with triisopropyl phosphite under reflux for 5 h. $(i\text{-}C_3H_7O)_2P(O)CH_2S(p\text{-}CH_3C_6H_4)$ was isolated and distilled under reduced pressure (bp 165 °C (0.1 Torr)). Yield: 88%. Infrared (thin film, cm^{-1}): 1254 (s, $\nu_{P=O}$), 994 (s, ν_{P-O-C}). ^{1}H NMR (CDCl$_3$): δ 7.4–7.1 (AA′**BB**′ quartet, C_6H_4, 4 H), 4.4–4.0 (m, OC*H*, 2 H), 3.09 (d, SCH_2P, $^2J_{PH}$ = 14.2 Hz), 2,28 (s, CH_3–Ph, 3 H), 1.31 (d, CH_3, 6 H, $^3J_{PH}$ = 6.2 Hz), 1.29 (d, CH_3, 6 H, $^3J_{PH}$ = 6.2 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 144.4 (s, SC_1), 137.3–127.5 (m, C_2, C_3, C_4), 71.8 (d, O*C*H, $^2J_{PC}$ = 6.5 Hz), 70.7 (d, O*C*H, $^2J_{PC}$ = 6.7 Hz), 29.7 (d, S*C*H$_2$P, $^1J_{PC}$ = 148.6 Hz), 23.7–21.9 (m, *C*H$_3$). ^{31}P{^{1}H} NMR (C_6H_6): δ 20.4.

The oxidation of $(i\text{-}C_3H_7O)_2P(O)CH_2S(p\text{-}CH_3C_6H_4)$ was accomplished by the same $KMnO_4/H_2SO_4$ oxidation reaction described above. The product was isolated as an oil, and ^{31}P NMR and mass spectroscopy indicated that the compound was pure. Yield: 27 g (63%). Infrared (thin film, cm^{-1}): 1323 (s, $\nu_{S=O\,asym}$), 1262 (s, $\nu_{P=O}$), 1157 (s, $\nu_{S=O\,sym}$), 994 (s, ν_{P-O-C}). NMR ^{1}H NMR: (CDCl$_3$): δ 7.9–7.2 (AA′**BB**′ quartet, C_6*H*$_4$, 4 H), 4.8–4.3 (m, O*C*H, 2 H), 3.72 (d, SCH_2P, 2 H, $^2J_{PH}$ = 16.8 Hz), 2.40 (s, CH_3–Ph, 3 H), 1.28 (d, CH_3, 12 H, $^3J_{PH}$ = 6.0 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 144.3 (s, S–C_1), 137.3 (s, C_4), 130.8–126.3 (m, C_2, C_3), 71.6 (d, O*C*H, $^2J_{PC}$ = 5.8 Hz), 54.1 (d, S*C*H$_2$P, $^1J_{PC}$ = 138.1 Hz), 25.0–20.7 (m, *C*H$_3$). ^{31}P{^{1}H} NMR (neat): δ 15.7. Anal. Calcd for $C_{14}H_{23}O_5PS$: C, 50.29; H, 6.93. Found: C, 50.72; H, 6.71.

$(i\text{-}C_3H_7O)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)$ (5). Diisopropyl ((*p*-tolylsulfinyl)methyl)phosphonate (**5**) was prepared by oxidation of diisopropyl ((*p*-tolylthio)methyl)phosphonate with sodium periodate. The procedure employed was similar to the one reported by Mikolajczyk.[13]

$(i\text{-}C_3H_7O)_2P(O)CH_2S(p\text{-}CH_3C_6H_4)$, 18.3 g (0.06 mol), was dissolved in a mixture of acetone (60 mL) and water (30 mL). Then 13.5 g (0.06 mol) of $NaIO_4$ was dissolved in 225 mL of water, and the solution was added dropwise to the mercaptide solution at 0–5 °C with constant stirring (addition time of 3 h). The reaction mixture was stirred at 0 °C for an additional 4 h. Sodium iodate was removed by filtration, and the filtrate was evaporated under reduced pressure to give $(i\text{-}C_3H_7O)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)$ as a colorless oil. Yield: 15.3 g, 90%.

Infrared (thin film, cm^{-1}): 1254 (s, $\nu_{P=O}$), 1052 (s, $\nu_{S=O}$), 1012, 987 (s, ν_{P-O-C}). ^{1}H NMR (CDCl$_3$): δ 7.69–7.26 (AA′BB′ quartet, C_6*H*$_4$, 4 H), 4.9–4.5 (m, OC*H*, 2 H), 3.32 (d, SCH_2P, 2 H, $^2J_{PH}$ = 15.0 Hz), 2.39 (s, CH_3–Ph, 3 H), 1.30 (d, *C*H$_3$, 12 H, $^3J_{PH}$ = 6.1 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): 141.5 (s, C_1), 130.9–121.5 (m, C_2, C_3, C_4), 71.3 (d, O*C*H, $^2J_{PC}$ = 6.6 Hz), 71.2 (d, O*C*H, $^2J_{PC}$ = 6.8 Hz), 55.7 (d, S*C*H$_2$P, $^1J_{PC}$ = 139.0 Hz), 25.3–20.5 (m, *C*H$_3$). ^{31}P{^{1}H} NMR (neat): δ 14.8.

$Ph_2P(O)CH_2S(O)_2NMe_2$ (9). A solution of lithium ((dimethylamino)sulfonyl)carbanion was prepared by treating *N′,N′*-dimethylaminomethanesulfonamide (6.3 g, 0.05 mol) with *n*-BuLi (0.05 mol) in THF (100 mL) as described by Corey.[14] The reaction mixture was cooled to −78 °C, and Ph_2PCl (11.3 g, 0.05 mol), in 100 mL of THF, was added dropwise (addition time of 30 min). The reaction mixture was slowly warmed to 25 °C and stirred overnight. The solvent was then evaporated under reduced pressure. The residue was extracted with

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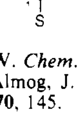
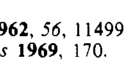
(10) Abbreviations used in the text include Me = methy, Et = ethyl, *i*-Pr = isopropyl, Bu = butyl, and THF = tetrahydrofuran. The numbering schemes for the rings are as shown:





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benzene (300 mL), and the LiCl was removed by filtration. A small aliquot was removed for analysis. $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ −26.6; Mass spectrum: *m/e* 307 (M^+). The filtrate was oxidized with $KMnO_4$ at 25 °C as described for **1**, except $MgSO_4$ was used instead of H_2SO_4, to yield the sulfonamide $(C_6H_5)_2P(O)CH_2S(O)_2N(CH_3)_2$ (mp 185 °C). Yield: 16.5 g, 100%. Mass spectrum (*m/e* (fragment), relative intensity): 324 (M^+) 2, 216 ($C_{13}H_{13}OP^+$) 69, 215 ($C_{13}H_{12}OP^+$) 100, 201 ($C_{12}H_{10}OP^+$) 12, 125 ($C_6H_5OS^+$) 8, 91 ($C_7H_7^+$) 26, 77 ($C_6H_5^+$) 18, 65 ($C_5H_5^+$) 13. Infrared (KBr, cm^{-1}): 1342 (s, $\nu_{S=O\,asym}$), 1198 (s, $\nu_{P=O}$), 1145 (s, $\nu_{S=O\,sym}$). ^1H NMR ($CDCl_3$): δ 7.9–7.4 (m, C_6H_5, 10 H), 4.07 (d, SCH_2P, 2 H, $^2J_{PH}$ = 10.2 Hz), 2.83 (s, N*Me*, 6 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 133.9–128.3 (m, C_6H_5), 50.5 (d, SCH_2P, $^1J_{PC}$ = 60.0 Hz), 37.3 (s, N*Me*). $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ 21.7. Anal. Calcd for $C_{15}H_{18}NO_3SP$: C, 55.72; H, 5.61; N, 4.33. Found: C, 55.91; H, 5.79; N, 4.37.

Preparation of the Complexes. Coordination complexes of the ligands were prepared by a single general procedure. The uranyl complexes were obtained by combining $UO_2(NO_3)_2{\cdot}6H_2O$ (2 mmol) in 15 mL of dry ethanol with ligand **1**, **3**, or **5** (4 mmol) in 25 mL of ethanol. The solution was mixed and the ethanol allowed to evaporate. The residual oils were washed with petroleum ether to remove unreacted ligand, and the complexes were recrystallized from a 1:1 mixture of CH_2Cl_2 and petroleum ether. The complex of ligand **9** was obtained in a similar fashion, except the ligand was initially dissolved in $CHCl_3$. The La(III) and Gd(III) complexes of ligand **5** were obtained in an identical fashion by using $La(NO_3)_3{\cdot}6H_2O$ and $Gd(NO_3)_3{\cdot}5H_2O$, and the Gd complex was formed in methanol.

Characterization of Complexes. $UO_2(NO_3)_2[(i\text{-}PrO)_2P(O)CH_2S(O)_2C_6H_{11}]_2$ (2). Infrared (KBr, cm^{-1}): 1314 (s, $\nu_{S=O\,asym}$), 1176 (s, $\nu_{P=O}$), 1146 (s, $\nu_{S=O\,sym}$), 1028 (s, ν_{P-O-C}), 1015 (s, ν_{P-O-C}), 943 (s, $\nu_{UO_2^{2+}}$). Anal. Calcd for $C_{26}H_{54}N_2O_{18}P_2S_2U$: C, 29.83; H, 5.20; N, 2.68. Found: C, 29.84; H, 5.61; N, 2.70.

$UO_2(NO_3)_2[(i\text{-}PrO)_2P(O)CH_2S(O)_2(p\text{-}CH_3C_6H_4)]_2$ (4). Infrared ($CHCl_3$, cm^{-1}): 1332 (m, $\nu_{S=O\,asym}$), 1178 (s, $\nu_{P=O}$), 1159 (s, $\nu_{S=O\,sym}$), 1023 (s, ν_{P-O-C}) 940 (m, $\nu_{UO_2^{2+}}$). Anal. Calcd for $C_{28}H_{46}N_2O_{18}S_2P_2U$: C, 31.64; H, 4.36; N, 2.64. Found: C, 32.25, H, 4.52; N, 2.65.

$UO_2(NO_3)_2[(i\text{-}PrO)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)]$ (6). Infrared ($CHCl_3$, cm^{-1}): 1190 (s, $\nu_{P=O}$), 1030–980 (s, $\nu_{S=O}$, ν_{P-O-C}), 940 (s, $\nu_{UO_2^{2+}}$). Anal. Calcd for $C_{14}H_{23}N_2O_{12}SPU$: C, 23.60; H, 3.25; N, 3.93. Found: C, 24.09; H, 3.42; N, 3.97.

$La(NO_3)_3[(i\text{-}PrO)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)]_2$ (7). Infrared ($CHCl_3$, cm^{-1}): 1204 (s, $\nu_{P=O}$), 1031 (s, $\nu_{S=O}$), 1018 (s, ν_{P-O-C}). Anal. Calcd for $C_{28}H_{46}N_3O_{17}S_2P_2La$: C, 34.97; H, 4.82; N, 4.37. Found: C, 34.51; H, 5.76; N, 5.07.

$Gd(NO_3)_3[(i\text{-}PrO)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)]{\cdot}H_2O$ (8). Infrared (KBr, cm^{-1}): 1204 (s, $\nu_{P=O}$), 1024 (s, $\nu_{S=O}$), 1006 (s, ν_{P-O-C}). Anal. Calcd for $C_{14}H_{25}N_3O_{14}SPGd$: C, 24.74; H, 3.71; N, 6.18. Found: C, 25.16; H, 4.10; N, 5.85.

$UO_2(NO_3)_2[Ph_2P(O)CH_2S(O)_2N(CH_3)_2]_2$ (10). Infrared (KBr, cm^{-1}): 1351 (s, $\nu_{S=O\,asym}$), 1161 (s, $\nu_{P=O}$), 1145 (s, $\nu_{S=O\,sym}$). Anal. Calcd for $C_{30}H_{36}N_4O_{14}S_2P_2U$: C, 34.62; H, 3.49; N, 5.38. Found: C, 35.25; H, 4.04; N, 5.07.

X-ray Diffraction Studies. Single crystals of **2** were obtained by slow evaporation of a 1:1 CH_2Cl_2/petroleum ether solution of the complex, and crystals of **8** were recovered from a 1:1 CH_2Cl_2/hexane solution. Attempts to obtain suitable crystals for the other complexes failed. Room-temperature data were collected by variable-speed θ–2θ scans on an Enraf Nonius CAD-4 diffractometer equipped with a graphite monochromator that used Mo Kα radiation. The structures were solved by using standard Patterson and difference Fourier methods and refined to the observed data ($I \geq 2\sigma(I)$) with full-matrix least-squares methods using appropriate neutral scattering factors and anomalous scattering terms.[15] Refinements included anisotropic thermal parameters for all non-hydrogen atoms and a correction for secondary extinction.[16] Final Fourier difference maps failed to show peaks that could be interpreted as hydrogen atoms. The Los Alamos Crystal Structure Codes[17] were used for all calculations. Data were corrected for absorption by using the relative intensity of a low-angle reflection measured as a function of Ψ (mapped to φ) multiplied by a spherical correction that used a radius calculated from the average distance between the three most prominent directions of crystal development. The function minimized was $R_F = \sum w^2[F_o - F_c]^2$ and weights were calculated as $w^2 = 4F^2/\sigma^2(I)$ where $\sigma(I) = \sigma_c(I) + (0.030I)^2$; $\sigma_c(1)$ is the error based on counting statistics. For the uranyl complex (space group $P2_1$), both enantiomorphs were refined. No significant difference was found for the *R* values, and no chemically meaningful difference was found in the metrical parameters. Lattice parameters are given in Table I. Atomic coordinates are listed in Tables

Table I. X-ray Data

	2	8
chem formula	$C_{26}H_{54}N_2O_{18}P_2S_2U$	$C_{14}H_{25}N_3O_{14}PSGd$
fw	1046.8	679.6
space group	$P2_1$	$P2_1/a$
a, Å	8.374 (4)	9.213 (3)
b, Å	25.423 (3)	21.09 (1)
c, Å	10.031 (2)	13.277 (6)
β, deg	100.49 (3)	98.36 (3)
V, Å^3	2099.9	2552.8
Z	2	4
ρ_{obsd}, g/cm^3	1.65	1.77
λ(Mo Kα_1), Å	0.709 30	0.709 30
T, °C	23	23
μ, cm^{-1}	39.0	28.1
transmission (min, max)	0.43–0.60	0.29–0.46
R_F	3.0	4.0
R_{wF}	3.8	5.4

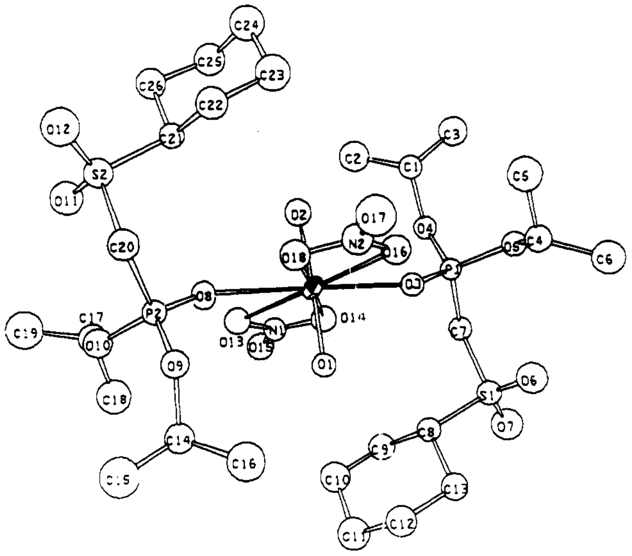

Figure 1. Molecular geometry and atom-labeling scheme for $UO_2(NO_3)_2[(i\text{-}C_3H_7O)_2P(O)CH_2S(O)_2(C_6H_{11})]_2$ (**2**).

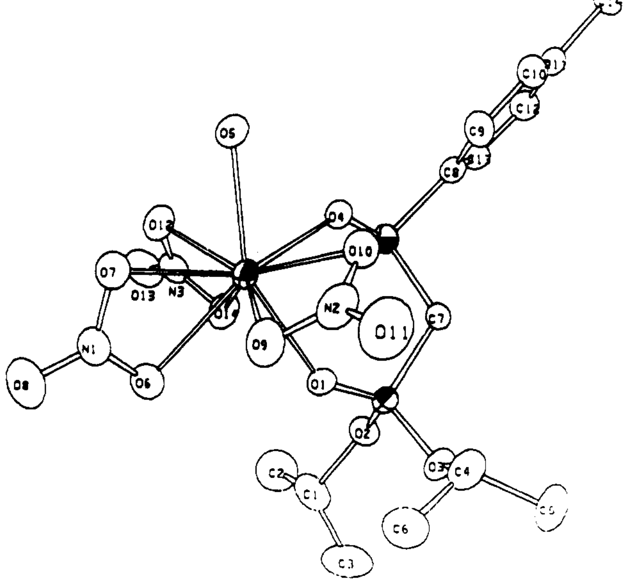

Figure 2. Molecular geometry and atom-labeling scheme for $Gd(NO_3)_3[(i\text{-}C_3H_7O)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)]{\cdot}H_2O$ (**8**).

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(15) (a) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Table 2.2A. (b) Cromer, D. T. *Ibid.*; Table 2.3.1.

(16) (a) Zachariasen, W. H. *Acta Crystallogr.* **1967**, *23*, 558–564. (b) Larson, A. C. *Ibid.* **1967**, *23*, 664–665.

(17) Larson, A. C. *Am. Crystallogr. Soc. Proc., Program Abstr. Bull. Ser. 2* **1977**, 67.

Table II. Fractional Coordinates for $UO_2(NO_3)_2[(i\text{-}C_3H_7O)P(O)CH_2S(O)_2(C_6H_{11})]_2$ (**2**)

atom	*x*	*y*	*z*	B^a
U(1)	0.22891 (4)	0.25000 (0)	0.41385 (4)	3.75
O(2)	0.028 (1)	0.2647 (4)	0.3319 (9)	6.0
P(1)	0.0960 (4)	0.1112 (1)	0.3719 (3)	4.2
C(1)	−0.204 (2)	0.147 (1)	0.266 (1)	5.2
C(3)	−0.315 (2)	0.106 (1)	0.190 (2)	8.1
C(4)	0.209 (2)	0.085 (1)	0.145 (1)	5.8
C(6)	0.263 (2)	0.030 (1)	0.113 (2)	10.1
S(1)	0.3698 (6)	0.0572 (2)	0.5657 (6)	5.8
O(7)	0.385 (1)	0.0169 (5)	0.667 (1)	9.6
C(9)	0.433 (2)	0.130 (1)	0.778 (2)	7.0
C(11)	0.706 (2)	0.168 (1)	0.844 (2)	8.5
C(13)	0.658 (2)	0.103 (1)	0.658 (2)	6.3
P(2)	0.3665 (4)	0.3916 (1)	0.4653 (3)	4.3
C(14)	0.670 (2)	0.366 (1)	0.583 (2)	6.2
C(16)	0.765 (2)	0.322 (1)	0.530 (3)	10.6
C(17)	0.250 (2)	0.415 (1)	0.694 (2)	7.6
C(19)	0.205 (3)	0.469 (1)	0.738 (2)	11.0
S(2)	0.1009 (5)	0.4526 (2)	0.2790 (5)	6.1
O(12)	0.093 (2)	0.4931 (5)	0.178 (2)	10.7
C(22)	0.038 (2)	0.383 (1)	0.069 (2)	6.5
C(24)	0.749 (3)	0.349 (1)	−0.013 (2)	10.3
C(26)	−0.196 (2)	0.410 (1)	0.185 (2)	6.8
N(1)	0.118 (2)	0.2375 (5)	0.678 (1)	4.4
O(15)	0.079 (1)	0.2322 (4)	0.785 (1)	8.0
N(2)	0.345 (2)	0.2657 (7)	0.15 (1)	6.9
O(18)	0.336 (2)	0.3035 (5)	0.234 (1)	6.5
O(1)	0.4294 (1)	0.2394 (3)	0.4963 (9)	4.5
O(3)	0.1948 (1)	0.1602 (3)	0.3745 (1)	5.0
O(4)	−0.0849 (1)	0.1194 (4)	0.3769 (9)	5.2
C(2)	−0.297 (2)	0.187 (1)	0.330 (2)	9.5
O(5)	0.103 (2)	0.0758 (5)	0.245 (1)	6.4
C(5)	0.110 (3)	0.115 (1)	0.028 (2)	11.3
C(7)	0.158 (1)	0.074 (1)	0.526 (1)	5.3
O(6)	0.421 (1)	0.0468 (5)	0.439 (1)	8.5
C(8)	0.475 (2)	0.114 (1)	0.642 (1)	5.4
C(10)	0.521 (2)	0.177 (1)	0.834 (2)	8.0
C(12)	0.752 (2)	0.153 (1)	0.715 (2)	7.5
O(8)	0.267 (1)	0.3456 (3)	0.463 (1)	4.7
O(9)	0.548 (1)	0.3819 (4)	0.4593 (9)	5.8
C(15)	0.773 (2)	0.412 (1)	0.628 (2)	8.9
O(10)	0.365 (1)	0.4234 (5)	0.596 (1)	6.1
c(18)	0.346 (2)	0.383 (1)	0.807 (2)	9.7
C(20)	0.310 (2)	0.433 (1)	0.316 (2)	5.8
O(11)	0.051 (1)	0.4648 (5)	0.406 (1)	8.0
C(21)	−0.006 (1)	0.396 (1)	0.202 (1)	4.8
C(23)	−0.064 (2)	0.335 (1)	0.009 (2)	9.0
C(25)	−0.286 (2)	0.362 (1)	0.131 (2)	8.2
O(13)	0.156 (2)	0.2831 (6)	0.632 (1)	6.5
O(14)	0.128 (2)	0.2006 (5)	0.596 (1)	6.0
O(16)	0.301 (2)	0.2214 (5)	0.196 (2)	6.6
O(17)	0.393 (2)	0.2724 (5)	0.049 (1)	12.0

[a] $100(U_{11} + U_{22} + U_{33})/3$. Anisotropic thermal parameters are given in the supplementary material.

II and III, and distances and angles are given in Tables IV and V. ORTEP projections with appropriate numbering schemes are given in Figures 1 and 2.

Results

The synthetic chemistry that has been developed for the ((alkylsulfonyl)methyl- and ((arylsulfonyl)methyl)phosphonates and ((arylsulfinyl)methyl)phosphonate is summarized in eq 1–5.

$$(RO)_3P + ClCH_2SR' \rightarrow (RO)_2P(O)CH_2SR' + RCl \quad (1)$$

$$R = i\text{-Pr}$$

$$R' = c\text{-}C_6H_{11},\ p\text{-}CH_3C_6H_4$$

$$(RO)_2P(O)CH_2SR' + KMnO_4 \xrightarrow[H_2SO_4]{C_6H_6} (RO)_2P(O)CH_2S(O)_2R' \quad (2)$$

$$R' = c\text{-}C_6H_{11}\ (\mathbf{1}),\ p\text{-}CH_3C_6H_4\ (\mathbf{3})$$

$$(RO)_2P(O)CH_2SR' + NaIO_4 \xrightarrow[H_2O]{(CH_3)_2CO} (RO)_2P(O)CH_2S(O)R' \quad (3)$$

$$R' = p\text{-}CH_3C_6H_4\ (\mathbf{5})$$

$$(C_6H_5)_2PCl + LiCH_2S(O)_2N(CH_3)_2 \xrightarrow{THF} (C_6H_5)_2PCH_2S(O)_2N(CH_3)_2 \quad (4)$$

$$(C_6H_5)_2PCH_2S(O)_2N(CH_3)_2 \xrightarrow[C_6H_6]{KMnO_4/MgSO_4} (C_6H_5)_2P(O)CH_2S(O)_2N(CH_3)_2 \quad (5)$$

The ((aminosulfonyl)methyl)phosphonate $(C_6H_5)_2P(O)CH_2S(O)_2N(CH_3)_2$ (**9**) in our hands could not be prepared by the procedure described in eq 2; therefore, an alternate scheme was sought. It was found that the ligand could be prepared in good yield as described in eq 4 and 5. The mass spectrum of **9** shows a parent ion consistent with the proposed formation.

Each of the (sulfonylmethyl)phosphonates (**1**, **3**, and **9**) is quite stable; however, attempts to isolate the desired sulfinyl derivatives were, unfortunately, frustrated by their tendency to disproportionate to the respective sulfide and sulfone. A similar observation for other sulfoxides was made by Mikolajczyk.[13] We were successful, however, in isolating $(i\text{-PrO})_2P(O)CH_2S(O)C_6H_4CH_3$ (**5**) in good yield from the periodate oxidation of the sulfide as described in eq 3. This ligand undergoes disproportionation at temperatures above 50 °C. Nonetheless, a parent ion was detected in the mass spectrum.

Previous studies have shown that bifunctional (carbamoylmethyl)phosphonates, under metal-loaded conditions, form bidentate complexes with uranyl nitrate and early lanthanide nitrates. Similarly, it is known that monofunctional phosphonates and pyridine *N*-oxides form stable complexes with UO_2^{2+} and Ln(III) ions, and we have recently shown that when these two

Table III. Fractional Coordinates for $Gd(NO_3)_3[(i\text{-}C_3H_7O)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)]\cdot H_2O$ (**8**)

atom	*x*	*y*	*z*	B^a	atom	*x*	*y*	*z*	B^a
Gd(1)	0.22429 (3)	0.46947 (2)	0.33405 (2)	4.19	P(1)	−0.0143 (2)	0.3645 (1)	0.1714 (1)	4.6
S(1)	0.0966 (2)	0.3122 (1)	0.3815 (1)	5.0	O(1)	0.0749 (5)	0.4215 (2)	0.2000 (3)	4.9
O(2)	0.0635 (5)	0.3141 (2)	0.1130 (4)	5.7	C(1)	0.1381 (10)	0.3332 (4)	0.0253 (7)	8.0
C(2)	0.274 (1)	0.2933 (8)	0.034 (1)	13.4	C(3)	0.038 (2)	0.3244 (9)	−0.0698 (8)	15.2
O(3)	−0.1620 (5)	0.3785 (3)	0.1007 (4)	5.7	C(4)	−0.2557 (8)	0.4345 (5)	0.1164 (7)	7.0
C(5)	−0.4104 (8)	0.4119 (6)	0.0767 (8)	9.3	C(6)	−0.204 (1)	0.4912 (6)	0.0592 (8)	9.2
C(7)	−0.0602 (7)	0.3227 (4)	0.2821 (5)	5.4	O(4)	0.1479 (5)	0.3782 (2)	0.4116 (3)	5.4
C(8)	−0.0035 (7)	0.2867 (3)	0.4791 (5)	4.3	C(9)	−0.0788 (8)	0.3310 (3)	0.5301 (6)	5.6
C(10)	−0.1511 (8)	0.3098 (4)	0.6082 (6)	5.7	C(11)	−0.1493 (7)	0.2465 (4)	0.6347 (5)	4.8
C(12)	−0.0758 (8)	0.2031 (4)	0.5811 (6)	5.6	C(13)	−0.0001 (8)	0.2233 (3)	0.5041 (5)	5.1
C(14)	−0.2289 (9)	0.2245 (5)	0.7239 (9)	7.7	O(5)	0.2559 (6)	0.5080 (3)	0.5042 (4)	6.7
O(6)	0.3409 (7)	0.5123 (3)	0.1990 (4)	7.0	N(1)	0.3938 (8)	0.5619 (4)	0.2460 (6)	7.5
O(7)	0.3730 (6)	0.5671 (3)	0.3370 (4)	6.6	O(8)	0.461 (1)	0.6016 (4)	0.2042 (6)	13.3
O(9)	0.0561 (6)	0.5556 (3)	0.2669 (5)	7.0	N(2)	−0.0492 (8)	0.5401 (4)	0.3110 (6)	6.7
O(10)	−0.0282 (5)	0.4937 (3)	0.3723 (4)	6.6	O(11)	−0.1671 (7)	0.5673 (4)	0.2947 (6)	10.8
O(12)	0.4831 (5)	0.4395 (3)	0.3921 (4)	6.6	N(3)	0.4923 (6)	0.3952 (4)	0.3305 (5)	5.9
O(13)	0.6082 (6)	0.3685 (3)	0.3257 (5)	9.0	O(14)	0.3739 (5)	0.3791 (3)	0.2751 (4)	6.6

[a] See footnote *a* in Table 11.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $UO_2(NO_3)_2[(i\text{-}C_3H_7O)_2P(O)CH_2S(O)_2(C_6H_{11})]_2$ (**2**)

U(1)–O(1)	1.752 (8)	U(1)–O(2)	1.774 (8)
U(1)–O(3)	2.325 (9)	U(1)–O(8)	2.489 (9)
U(1)–O(13)	2.52 (1)	U(1)–O(14)	2.49 (1)
U(1)–O(16)	2.48 (1)	U(1)–O(18)	2.54 (1)
S(1)–O(6)	1.43 (1)	S(1)–O(7)	1.43 (1)
S(1)–C(7)	1.80 (1)	S(1)–C(8)	1.80 (1)
S(2)–O(11)	1.45 (1)	S(2)–O(12)	1.44 (1)
S(2)–C(20)	1.80 (1)	S(2)–C(21)	1.79 (1)
P(1)–O(3)	1.49 (1)	P(1)–O(4)	1.538 (9)
P(1)–O(5)	1.57 (1)	P(1)–C(7)	1.81 (1)
P(2)–O(8)	1.432 (9)	P(2)–O(9)	1.549 (9)
P(2)–O(10)	1.54 (1)	P(2)–C(20)	1.82 (1)
O(6)–S(1)–C(7)	106.8 (7)	O(7)–S(1)–C(7)	106.7 (7)
C(7)–S(1)–C(8)	106.6 (7)	O(6)–S(1)–O(7)	119.6 (9)
O(6)–S(1)–C(8)	108.9 (7)	O(7)–S(1)–C(8)	107.6 (8)
O(11)–S(2)–C(20)	107.8 (7)	O(12)–S(2)–C(20)	105.2 (7)
C(20)–S(2)–C(21)	105.1 (7)	O(11)–S(2)–O(12)	119.1 (9)
O(11)–S(2)–C(21)	110.3 (7)	O(12)–S(2)–C(21)	108.5 (8)
O(3)–P(1)–O(4)	115.7 (5)	O(3)–P(1)–O(5)	113.1 (6)
O(3)–P(1)–C(7)	110.4 (6)	O(4)–P(1)–O(5)	106.5 (6)
O(4)–P(1)–C(7)	100.0 (5)	O(5)–P(1)–C(7)	110.3 (7)
O(8)–P(2)–O(9)	116.0 (6)	O(8)–P(2)–O(10)	110.4 (6)
O(8)–P(2)–C(20)	113.3 (6)	O(9)–P(2)–O(10)	106.1 (6)
O(9)–P(2)–C(20)	99.7 (6)	O(10)–P(2)–C(20)	110.7 (7)

Table V. Selected Bond Distances (Å) and Angles (deg) for $Gd(NO_3)_3[(i\text{-}C_3H_7O)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)]\cdot H_2O$ (**8**)

Gd(1)–O(1)	2.319 (4)	Gd(1)–O(4)	2.340 (5)
Gd(1)–O(5)	2.378 (5)	Gd(1)–O(6)	2.397 (5)
Gd(1)–O(7)	2.470 (6)	Gd(1)–O(9)	2.468 (6)
Gd(1)–O(10)	2.505 (5)	Gd(1)–O(12)	2.479 (5)
Gd(1)–O(14)	2.542 (5)	S(1)–O(4)	1.506 (5)
S(1)–C(7)	1.823 (7)	S(1)–C(8)	1.779 (7)
P(1)–O(1)	1.475 (5)	P(1)–O(2)	1.551 (5)
P(1)–O(3)	1.565 (5)	P(1)–C(7)	1.815 (7)
O(4)–S(1)–C(7)	105.3 (3)	C(7)–S(1)–C(8)	97.1 (3)
O(4)–S(1)–C(8)	105.2 (3)	O(1)–P(1)–O(2)	114.0 (3)
O(1)–P(1)–O(3)	113.8 (3)	O(1)–P(1)–C(7)	112.0 (3)
O(2)–P(1)–O(3)	104.7 (3)	O(2)–P(1)–C(7)	104.6 (3)
O(3)–P(1)–C(7)	107.1 (3)		

coordinating functionalities are combined in a single ligand with the P=O and N—O oxygen atoms in 1,3-positions, then the bidentate ligand complexes $UO_2(NO_3)_2[(RO)_2P(O)C_5H_4NO]$[3] and $Ln(NO_3)_3[(RO)_2P(O)C_5H_4NO]_2$[4] are isolated. It is also known that monofunctional organosulfinyl ligands form a variety of complexes with uranyl ion and Ln(III) ions, and in the present study, a ligand design question was posed. Can ligands containing both phosphoryl and sulfinyl or sulfonyl functional groups form complexes with UO_2^{2+} and Ln(III) ions?

The coordination chemistry of each of the ligands **1**, **3**, **5**, and **9** with $UO_2(NO_3)_2$ and of **5** with La(III) and Gd(III) was examined. Complexes were prepared under conditions in which there was enough ligand present to form at least a bis complex. The complexes isolated from these studies had the following compositions, $UO_2(NO_3)_2(\mathbf{1})_2$, $UO_2(NO_3)_2(\mathbf{3})_2$, $UO_2(NO_3)_2(\mathbf{9})_2$, $U(NO_3)_2(\mathbf{5})$, $La(NO_3)_3(\mathbf{5})_2$, and $Gd(NO_3)_3(\mathbf{5})\cdot H_2O$, as deduced from elemental analyses. Suitable single crystals of two complexes, $UO_2(NO_3)_2[(i\text{-}C_3H_7O)_2P(O)CH_2S(O)_2C_6H_{11}]_2$ (**2**) and $Gd(NO_3)_3[(i\text{-}C_3H_7O)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_9)]\cdot H_2O$ (**8**), were obtained, and the molecular structures were determined by single-crystal X-ray analysis. The results are presented below, following discussion of spectroscopic data.

Discussion

Syntheses. Preparations for selected (sulfidomethyl)phosphonates, $(RO)_2P(O)CH_2SR'$, (sulfinylmethyl)phosphonates, $(RO)_2P(O)CH_2S(O)R'$, and (sulfonylmethyl)phosphonates, $(RO)_2P(O)CH_2S(O)_2R'$, have been reported previously, and they have been used primarily as reagents in combination with ketones to obtain α,β-unsaturated sulfides, sulfoxides, and sulfones.[12,13] Surprisingly, neither the coordination chemistry nor the extraction properties of these compounds have been studied. We have extended the briefly described synthetic routes to include examples of the above compounds with hydrophobic R and R′ groups that might have useful coordination properties as well as applications in liquid–liquid extractions. In particular, ligands with large R′ groups were sought. In addition, syntheses for ((aminosulfinyl)methyl)phosphonates $(RO)_2P(O)CH_2S(O)NR'_2$, and ((aminosulfinyl)methyl phosphine oxides, $R_2P(O)CH_2S(O)NR'_2$, were sought since these compounds should provide electronic parallels with the corresponding (carbamoylmethyl)phosphonates, $(RO)_2P(O)CH_2C(O)NR'_2$, and carbamoylmethyl phosphine oxides, $R_2P(O)CH_2C(O)NR'_2$. In particular, it was expected that the sulfinyl oxygen atom might provide a stronger oxygen donor site than the carbamoyl oxygen atom, and this, in turn, should alter coordination complex structures and extraction behavior.

The procedure for the preparation of the (thiomethyl)phosphonates $(i\text{-}C_3H_7O)_2P(O)CH_2S(c\text{-}C_6H_{11})$ and $(i\text{-}C_3H_7O)_2P(O)CH_2S(p\text{-}CH_3C_6H_4)$ (eq 1) is similar to that described by Shahak.[12] The compounds were fully characterized and found to have anticipated spectroscopic properties. The sulfides were subsequently oxidized with $KMnO_4\text{–}H_2SO_4/C_6H_6$ as described in eq 2. The (sulfonylmethyl)phosphonates **1** and **3** were isolated in good yields as a solid and a distilled liquid, respectively. Compound **3** shows a parent ion in the mass spectrum, while **1** does not. Both compounds show the presence of $M + 1^+$ and/or $M + 2^+$ ions as well as anticipated fragment ions.

Spectroscopic Data and Assignments. The infrared spectra of **1** and **3** display two bands that are assigned to the asymmetric and symmetric sulfone stretches, ν_{SO_2}: **1**, 1314 and 1144 cm^{-1}; **3**, 1323 and 1157 cm^{-1}. These frequencies compare favorably with those reported for various organosulfones.[18] The (sulfonylmethyl)phosphonates also show a distinct, strong phosphoryl stretch, ν_{PO}: **1**, 1259 cm^{-1}; **3**, 1262 cm^{-1}. These frequencies compare with those reported for (carbamoylmethyl)phosphonates[2] and (*N*-oxopyridyl)phosphonates.[3] The $^{31}P\{^1H\}$ NMR spectra for **1** and **3** show single resonances at δ 10.8 and 15.7 that are in the region expected for organophosphonates.[19] The $^{13}C\{^1H\}$ and ^1H NMR spectra were assigned, and the data are consistent with the proposed structures. The shifts and coupling constants for the methyl carbon atom spanning the P=O and $S(O)_2$ groups are of particular interest: **1**, ^1H δ 3.53 (J_{PH} = 16.8 Hz); $^{13}C\{^1H\}$ δ 48.2 (J_{PC} = 139.6 Hz); **3** ^1H δ 3.72 (J_{PH} = 16.8 Hz), $^{13}C\{^1H\}$ δ 54.1 (J_{PC} = 138.1 Hz). The methyl carbon atom is prochiral, and an AB quartet would be expected to appear on each member of the doublet in the ^1H NMR spectra. This coupling was not resolved, and it is assumed that there is accidental chemical shift equivalency for the two protons on this carbon atom. These results can be compared with corresponding data for $(C_2H_5O)_2P(O)CH_2C(O)OC_2H_5$: ^1H δ 2.93 (J_{PH} = 23.0 Hz); $^{13}C\{^1H\}$ δ 34.4 (J_{PC} = 131.8 Hz).[20]

The infrared spectrum of ligand **9** shows two bands in the ν_{SO_2} region, 1342 and 1145 cm^{-1}, and a single band for the phosphoryl stretch, 1198 cm^{-1}. The last mode appears shifted significantly down-frequency from the corresponding frequencies in $(i\text{-}PrO)_2P(O)CH_2C(O)NEt_2$,[21] 1253 cm^{-1}, and $Ph_2P(O)CH_2C(O)NEt_2$,[22] 1206 cm^{-1}. This observation suggests that the P=O group in **9** may be less basic than those in the CMP ligands, and this feature will be quantitatively assessed in liquid–liquid extractions planned in the future. The $^{31}P\{^1H\}$ NMR spectrum for **9** displays a singlet, δ 21.7, and this resonance is shifted slightly

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upfield of the resonance in $Ph_2P(O)CH_2C(O)NEt_2$, δ 27.9,[22] but it is comparable to that found for $(i\text{-}PrO)_2P(O)CH_2C(O)NEt_2$, δ 22.[21]

The infrared spectrum of ligand **5** shows a band at 1052 cm^{-1}, which is assigned to the sulfoxide stretch ν_{SO}, and a band at 1254 cm^{-1}, which is assigned to the phosphoryl stretch ν_{PO}. It is interesting to note that the latter frequency is only slightly downfrequency of the phosphoryl stretch in sulfone **3**. This suggests that, for **3** and **5**, the change in sulfur oxidation state apparently does not dramatically alter the electron density and, therefore, probably not the base strength of the P=O group. The ^{31}P NMR spectrum for **5** shows a singlet at δ 14.8, and the proton and ^{13}C resonances for the methyl group spanning the P(O) and S(O) functional groups are simple and first order: ^1H, δ 3.32 (J_{PH} = 15.0 Hz); ^{13}C δ 55.7 (J_{PC} = 139.0 Hz). The corresponding data for $(i\text{-}PrO)_2P(O)CH_2C(O)NEt_2$ are as follows: $^{31}P\{^1H\}$, δ 22.0; ^1H, δ 2.86 (J_{PH} = 22 Hz); $^{13}C\{^1H\}$, δ 34.8 (J_{PC} = 133.6 Hz).

The results from X-ray diffraction structural analyses presented below may be used to help interpret spectroscopic data collected for the coordination complexes and to tentatively deduce structures for the complexes on which X-ray diffraction analyses were not possible. The infrared spectra of the uranyl (sulfonylmethyl)phosphonate complexes $UO_2(NO_3)_2[(i\text{-}PrO)_2P(O)CH_2S(O)_2C_6H_{11}]_2$ (**2**), $UO_2(NO_3)_2[(i\text{-}PrO)_2P(O)CH_2S(O)_2(p\text{-}CH_3C_6H_4)]_2$ (**4**), and $UO_2(NO_3)_2[(C_6H_5)_2P(O)CH_2S(O)_2N(CH_3)_2]_2$ (**10**) show a single phosphoryl stretch at 1176, 1178, and 1161 cm^{-1}, respectively. The positions of these bands correspond to coordination shifts of $\Delta\nu_{PO}$ = 83, 76, and 37 cm^{-1}, with respect to the free ligands. These shifts fall on the high and low ends of the range of shifts typically observed for uranyl complexes of bifunctional phosphonate ligands.[2-4] To the degree that coordination shifts may be used to infer ligand donor strengths, the small coordination shift in **10** is consistent with the deduction presented above that, on the basis of the low phosphoryl stretching frequency in the free ligand **9**, the donor strength of the aminosulfonyl ligand appears to be smaller than the donor strength of the alkylsulfonyl, arylsulfonyl, and carbamoyl ligands.

Two other bands, which can be assigned to sulfone stretches, are also observed: **2**, 1314 and 1146 cm^{-1}, **4**, 1332 and 1159 cm^{-1}; **10**, 1351 and 1145 cm^{-1}. These are essentially unshifted or shifted to slightly higher frequency compared to the bands for the respective free ligands. This observation in **2** is consistent with the fact that the sulfone oxygen atoms are not bonded to the uranyl group as revealed by the crystal structure determination. The asymmetric uranyl stretches for the three complexes appear in the range 944–940 cm^{-1}, and they are identical with that found for $UO_2(NO_3)_2[(i\text{-}PrO)_2P(O)CH_2C(O)NEt_2]$.[23] The infrared spectra and the analytical data for the three uranyl complexes are clearly consistent with the conclusion that two (sulfonylmethyl)phosphonate ligands bond to uranyl via the phosphoryl oxygen and the sulfone groups remain uncoordinated. Unfortunately, the NMR data for these complexes provide no further definitive information related to the ligand conformations in the solution structures. Attempts to obtain lanthanide complexes of the (sulfonylmethyl)phosphonates led to mixtures that have not been successfully separated and characterized.

The infrared spectra for the (sulfinylmethyl)phosphonate complexes **6**–**8** show a strong band at 1190, 1204, and 1204 cm^{-1}, respectively, that can be assigned to a coordinated phosphoryl group. The positions of these bands represent coordination shifts of 64, 50, and 50 cm^{-1}, respectively, and the shifts are comparable to those found for uranyl and lanthanide complexes of $(i\text{-}PrO)_2P(O)CH_2C(O)NEt_2$.[21,23] In addition, a single band is found that can be tentatively assigned to the sulfoxide stretch:[24] **6**, ~1000 cm^{-1}; **7**, 1031 cm^{-1}; **8**, 1024 cm^{-1}. These represent coordination shifts of ~50, 21, and 28 cm^{-1}. The sulfoxide coordination shifts for the lanthanide complexes are relatively small in comparison to those found for uranyl and Ln(III) complexes (80–120 cm^{-1}) of monofunctional alkyl sulfoxides.[7,8] Nonetheless, relatively small carbamoyl coordination shifts also have been found in several lanthanide–CMP complexes where bidentate ligand binding has been demonstrated by X-ray analysis.[21,23] The asymmetric uranyl stretch, 940 cm^{-1} for **6**, is comparable to that reported for the uranyl complex of $(C_6H_5)_2SO$ but higher than for the uranyl complex of $(CH_3)_2SO$.[7] On the basis of the elemental analyses, infrared coordination shifts, and the molecular structure determination for **8**, it is concluded that the (sulfinylmethyl)phosphonate ligand **5** acts as a bidentate ligand in all three complexes.

Structure Studies of Complexes: $UO_2(NO_3)_2[(i\text{-}C_3H_7O)_2P(O)CH_2S(O)_2C_6H_{11}]_2$ (2) and $Gd(NO_3)_3[(i\text{-}PrO)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)]\cdot H_2O$. Views of the molecules are shown in Figures 1 and 2, respectively.

The structure of the uranyl (sulfonylmethyl)phosphonate complex **2** confirms that the uranyl ion is bonded to two bidentate nitrate ions and the phosphoryl oxygen atoms of two trans, monodentate $[(i\text{-}PrO)_2P(O)CH_2S(O)_2C_6H_{11}]$ ligands. The sulfone oxygen atoms are pointed away from the uranyl ion. The resulting coordination polyhedron about uranium is typical of that found in other bis(ligand)uranyl nitrate complexes. Selected structural parameters for **2** are summarized in Table IV, and they are similar to those encountered for other uranyl phosphonate complexes. The uranyl group is essentially linear, O–U–O = 176.6 (5)°, and the average U=O bond distance, 1.763 (8) Å, falls within a range of U=O distances reported for a variety of uranyl complexes containing trans, monodentate and cis, bidentate phosphonate ligands.[3] In particular, it is useful to compare the distance in **2** with the distance in $UO_2(NO_3)_2[(C_4H_9O)_3P(O)]_2$, 1.742 (7) Å, in which the two monofunctional phosphonate ligands are in trans positions.[25]

The U–O(phosphoryl) distances for **2** are unexpectedly different: U–O(3) = 2.325 (9) Å and U–O(8) = 2.489 (9) Å. These distances span the range of distances found in structures of several uranyl complexes with bidentate phosphonate ligands,[3] and they may also be compared with the distance in $UO_2(NO_3)_2[(C_4H_9O)_3P(O)]_2$, 2.347 (6) Å. The P=O distances in **2**, 1.49 (1) and 1.432 (9) Å, are also significantly different. As expected, the long P=O distance is associated with the ligand displaying the shorter U—O distance. These P=O distances also may be compared with the P=O distance in $UO_2(NO_3)_2[(C_4H_9O)_3P(O)]_2$, 1.489 (7) Å. It is noteworthy that the distances P(1)–C(7) and P(2)–C(20) are identical, 1.81 (1) and 1.82 (1) Å, despite the differences in P=O distances in the two ligands. The average U–O (nitrate) bond distance, 2.51 Å (range 2.54(1)–2.48 (1) Å), is similar to those found in $UO_2(NO_3)_2\cdot 2H_2O$ and a number of uranyl nitrate phosphonate complexes.[3,22,23,25]

The molecular structure of the gadolinium complex **8** confirmed the proposed composition, $Gd(NO_3)_3[(i\text{-}PrO)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)]\cdot H_2O$. It also revealed a unique structure compared to those previously reported for lanthanide complexes of the (carbamoylmethyl)phosphonates and phosphinopyridine *N,P*-dioxides. In the case of **8**, the Gd(III) ion is bonded to three bidentate nitrate ions, *one bidentate* neutral (sulfinylmethyl)phosphonate ligand, and a water molecule. These ligands provide a total coordination number of 9. With other bifunctional ligands, we have observed that early lanthanides typically bind to two bidentate bifunctional ligands and no water is found in the complex.[22,23] With later lanthanides, the (carbamoylmethyl)phosphonates bind with two ligands in a monodentate mode and a water molecule is also found bonded to the lanthanide.[23] Unfortunately, no closely comparable structures for Gd(III) complexes have been reported, so the present structure appears unique. The Gd–O(1)(phosphoryl) and Gd–O(4) sulfoxide bond distances, 2.319 (4) and 2.340 (5) Å, are similar, and they may be compared to distances in $Sm(NO_3)_3[(i\text{-}PrO)_2P(O)CH_2C(O)NEt_2]_2$, Sm–O(phosphoryl)[23] = 2.418 (3) Å, $Nd(NO_3)_3[Ph_2P(O)CH_2C(O)NEt_2]_2$, Nd–O(phosphoryl)[22] = 2.456 (4) Å, and $Yb(NO_3)_3[(C-$

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$H_3)_2SO]_3$, Yb-O(sulfoxide) = 2.24 (3) Å. The short distances in **8**, relative to the Ln-O(P) distances in the 10-coordinate complexes, are expected due to the lower coordination number in **8**. Further, the difference in 9-coordinate radii between Gd(III) (1.247 Å) and Yb(III) (1.182 Å) accounts for much of the difference in Ln-O(S) bond distances between **8** and $Yb(NO_3)_3[(CH_3)_2SO]_3$. The Gd-O(5)(water) bond distance, 2.378 (5) Å, appears to be normal. The average Gd-O(nitrate) distance, 2.477 Å (range 2.397-2.542 Å), also is similar to those found in other gadolinium nitrate structures.

Conclusion

It has been shown in this study that several (sulfonylmethyl)phosphonates may be easily prepared and purified, and the synthesis developed is sufficiently general that it would be applicable to formation of numerous derivatives. Coordination chemistry of these ligands with the uranyl ion revealed that, unlike that in (carbamoylmethyl)phosphonates, only monodentate binding through the phosphoryl oxygen atom was realized. Synthesis and stabilization of (sulfinylmethyl)phosphonates proved to be more difficult. In fact, the close analogue with the CMP ligand family $(RO)_2P(O)CH_2S(O)NEt_2$ could not be isolated. The coordination chemistry of $(i\text{-}C_3H_7O)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)$ with uranyl ion resulted in the formation of a complex **8** in which the ligand was bonded in a bidentate fashion. With the lanthanides La and Gd bidentate bonding modes were also deduced, but unlike CMP-lanthanide complexes, only one ligand was found bonded to the lanthanide ion. Clearly, there are several features that distinguish these ligands from the CMP family. Unfortunately, the instability of the known derivatives toward disproportionation makes these ligands useless for practical liquid-liquid extraction. We are, however, presently engaged in attempts to reduce this decomposition tendency by variations in steric and electronic effects on the (sulfinylmethyl)phosphonate backbone.

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Registry No. **1**, 120991-41-5; **2**, 121029-36-5; **3**, 120991-42-6; **4**, 121011-75-4; **5**, 120991-43-7; **6**, 121011-76-5; **7**, 121011-77-6; **8**, 121011-78-7; **9**, 120991-44-8; **10**, 121011-79-8; $ClCH_2S(C_6H_{11})$, 68483-71-6; $(i\text{-}C_3H_7O)_3P$, 116-17-6; $(i\text{-}C_3H_7O)_2P(O)CH_2S(C_6H_{11})$, 120991-45-9; $(i\text{-}C_3H_7O)_2P(O)CH_2S(p\text{-}CH_3C_6H_4)$, 120991-46-0; $ClCH_2S(p\text{-}CH_3C_6H_4)$, 34125-84-3; Ph_2PCl, 1079-66-9; lithium ((dimethylamino)sulfonyl)carbanion, 61669-75-8.

Supplementary Material Available: Tables SI-SVI, listing additional characterization data and complete X-ray data, anisotropic thermal parameters, and bond angles and distances (11 pages); tables of calculated and observed structure factors (29 pages). Ordering information is given on any current masthead page.

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Influence of π-Donation on *N*-Methyl Group Exchange in Zirconocene *N*,*N*-Dimethyldithiocarbamates and *N*,*N*-Dimethylthiocarbamates

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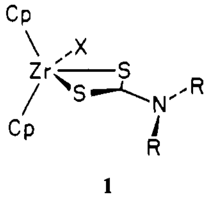
The kinetics of *N*-methyl group exchange in zirconocene *N*,*N*-dimethyldithiocarbamates, $Cp_2ZrX(Me_2dtc)$ (X = Cl, Br, I, Me, CH_2SiMe_3, CH_2CMe_2Ph, CH_2Ph, OPh, Opy (4-hydroxypyridinate), OXyl (2,6-dimethylphenoxide)), and *N*,*N*-dimethylthiocarbamates, $Cp_2ZrX(Me_2mtc)$ (X = Cl, Opy), have been studied by variable-temperature ^1H NMR spectroscopy. For the $Cp_2ZrX(Me_2dtc)$ complexes, rates and activation parameters are relatively independent of the nature of the monodentate ligand when X = halide or alkyl ($k(25\ ^\circ C) = 1\text{-}25\ s^{-1}$; $\Delta H^\ddagger = 14\text{-}17$ kcal/mol), but there is a dramatic increase in rate as the π-donating ability of X varies in the order Cl < Opy < OPh; $k(25\ ^\circ C) = 1.0 \times 10^4\ s^{-1}$ and $\Delta H^\ddagger = 9.8$ kcal/mol when X = OPh. No dramatic increase in exchange rate is observed for $Cp_2ZrX(Me_2mtc)$ as X varies from Cl to Opy. Except for the aryloxy dithiocarbamate complexes, rates and activation parameters are similar to those for related organic dithiocarbamates and thiocarbamates, strongly suggesting a mechanism involving rotation about the $C{=}N$ bond. $Cp_2ZrX(Me_2dtc)$ (X = OPh, Opy) is believed to exchange methyl groups by a Zr-S bond-rupture mechanism. This mechanism, which is promoted by the π-donor properties of the aryloxy ligands, is inaccessible in aryloxythiocarbamate complexes because it would give a higher energy, unobserved stereoisomer. Preparative methods for the $Cp_2ZrX(Me_2dtc)$ and $Cp_2ZrX(Me_2mtc)$ complexes and the $Cp_2Zr(X)Cl$ intermediates are described.

Introduction

Chlorozirconocene dithiocarbamate complexes, $Cp_2ZrCl(RR'dtc)$ ($Cp = \eta^5\text{-}C_5H_5$; $RR'dtc = S_2CNRR'$),[2-4] are interesting examples of fluxional, 18-electron, titanium group metallocenes. An X-ray study[5] of the *N*,*N*-diethyl derivative, $Cp_2ZrCl(Et_2dtc)$, has established the expected bent metallocene structure **1**, with the Zr atom, Cl atom, and the two S atoms of the planar, bidentate dithiocarbamate ligand in the quasi-mirror plane that bisects the Cp-Zr-Cp angle. One interesting facet of this structure is considerable crowding in the $ZrClS_2C_{10}$ coordination group as evidenced by very short nonbonded contacts and unusually long Zr-Cl and Zr-S bond lengths. The Zr-Cl distance is 2.556 (2) Å, 0.12 Å longer than that in Cp_2ZrCl_2,[6] and the bond length to the lateral S atom is 2.723 (2) Å, 0.09 Å longer than the more normal bond to the interior S atom.



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A ^1H NMR study[5] of the *N*,*N*-dimethyl derivative, $Cp_2ZrCl(Me_2dtc)$, has shown that the inequivalent *N*-methyl

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