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Oxidative Decarbonylation of Metal Carbonyls as a Route to Novel Metal Sulfur and Selenium Compounds. Structure of [(C6H5)4P]3[Cr(S2CO)3]

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The reactions of $M(CO)_6$ (M = Cr, Mo, W) with soluble polysulfides and polyselenides in dimethylformamide (DMF) has been investigated. Both $Mo(CO)_6$ and $W(CO)_6$ readily undergo oxidative decarbonylation in the presence of polysulfide or polyselenide to generate MS_4^{2-} and MSe_4^{2-}, respectively, in good yields. Investigations of the reaction solutions by IR spectroscopy give evidence of an intermediate containing a polychalcogenide ring chelated to a metal tetracarbonyl dianion. Reaction of $Cr(CO)_6$ with polyselenide solution also results in complete oxidative decarbonylation but apparently produces an unidentified mixture of higher chromium selenides. Reaction of $Cr(CO)_6$ with polysulfide solution generates the novel tris(dithiocarbonate) complex [Cr-$(S_2CO)_3]^{3-}$. This was isolated in good yield as the $(C_6H_5)_4P^+$ salt and characterized by X-ray crystallography. The cell is triclinic, $P\bar{1}$, with $a = 13.149$ (5) Å, $b = 13.662$ (5) Å, $c = 20.327$ (5) Å, $\alpha = 92.36(3)°$, $\beta = 94.77(3)°$, $\gamma = 115.46(3)°$, $V = 3274$ Å^3, $Z = 2$, $R = 0.0445$, and $R_w = 0.0360$. This compound reacts with elemental sulfur to produce unidentified chromium sulfides. However, there is no spectral evidence that dithiocarbonates are intermediates in any of the other oxidative decarbonylation reactions.

Introduction

The chemistry of molybdenum and tungsten sulfides is quite extensive.[1-3] Much of this development is due to the presence of molybdenum–sulfur clusters in electron-transfer enzymes,[4] as well as the use of molybdenum and tungsten sulfides as components in hydrodesulfurization catalysts.[5] Molybdenum in particular, has a very high affinity for sulfur in a variety of oxidation states and will form a large number of unusual clusters.[6] The fundamental building blocks in this chemistry are the tetrathiometalates (MS_4^{2-}), which can be easily made in good yield.[7] They can act as ligands and coordinate to other metals through the sulfur atoms or undergo a variety of complex redox reactions to form sulfur-rich clusters. The selenium analogues are considerably less well-known. This is probably due to the perception that their chemistry is similar to that of sulfides. Also, the starting material, H_2Se, is expensive, inconvenient, and toxic. However, some workers have recently begun to explore the coordination chemistry and the internal redox chemistry of the metal tetraselenometalates,[8-10] finding in many cases that the chemistry is significantly different from that of the sulfides.

We have recently reported a convenient method of preparing tetraselenomolybdate and -tungstate from metal carbonyls and soluble polyselenides and illustrated their use in forming new binary metal selenides.[11] Unlike polytelluride anions, which chelate to metal carbonyl fragments,[12] polyselenides oxidize the metal to the M^{6+} oxidation state with loss of all carbonyls. The oxidative decarbonylation reaction is useful because it avoids the use of noxious H_2Se and uses cheap, readily available materials instead. In this paper, we report fully on this unusual reaction, its extension to soluble polysulfides, and reactions with $Cr(CO)_6$ to form a novel tris(dithiocarbonato)chromate(III) complex. This is the first homoleptic dithiocarbonate and is the first prepared in this manner. It should be noted that, to our knowledge, no soluble binary chromium sulfides have been characterized and only one chromium selenide, $Cr_3Se_{24}^{3-}$,[13] has been characterized.

Experimental Section

All reagents were purchased from Strem Chemical Co. and used as obtained. Solvents were Aldrich Gold Label and were thoroughly degassed with purified argon and stored over activated sieves before use. Since all the compounds under investigation are air sensitive, solids were handled in a glovebox. Reactions were routinely carried out with the use of standard Schlenk techniques under an atmosphere of purified argon. Microanalyses were performed by Atlantic Microlab, Norcross, GA, or Galbraith Laboratories, Knoxville, TN. Selenium analyses were performed gravimetrically.[14] The polyselenide reagent K_2Se_3 was prepared as previously described,[11] and the polysulfide analogue was prepared by an identical procedure.

Preparation of [(C6H5)4P]2[WSe4]. In a typical reaction, 0.25 g of K_2Se_3 (0.79 mmol), 0.28 g of $W(CO)_6$ (0.79 mmol), and 0.65 g of $(C_6H_5)_4PBr$ (1.55 mmol) were dissolved in 10 mL of DMF, and the solution was stirred for 0.5 h. During this time the solution color changed from green-brown to dark red. The solution was then heated to 100 °C with stirring for 1 h. The resulting bright cherry red solution was filtered, and 10 mL of THF was layered onto the solution. Upon storage at 4 °C overnight, a large crop of orange crystalline product could be isolated (0.55 g; 60% yield). These crystals were suitable for X-ray structural analysis. Anal. Calcd for $C_{48}H_{40}P_2Se_4W$: C, 48.32; H, 3.42; Se, 26.81. Found: C, 45.32; H, 3.37; Se, 26.11.

Preparation of [(C6H5)4P]2[MoSe4]. In a fashion similar to the above reaction, 0.25 g of K_2Se_3 (0.79 mmol), 0.20 g of $Mo(CO)_6$ (0.76 mmol), and 0.65 g of $(C_6H_5)_4PBr$ (1.55 mmol) were combined in 10 mL of DMF with stirring. The mixture was heated for 0.5 h, after which time it turned bright blue. It was filtered and layered with THF, and this mixture was stored at 4 °C overnight, depositing large blue needles of product (0.24 g; 55% yield). Anal. Calcd for $C_{48}H_{40}MoP_2Se_4$: C, 52.81; H, 3.69; Se, 28.99. Found: C, 51.17; H, 3.79; Se, 27.43. Note: we consistently obtained combustion analyses that were low in carbon for

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Table I. Crystallographic Data for [(C₆H₅)₄P]₃[Cr(S₂CO)₃]

chem formula C₇₅H₆₀O₃CrP₃S₆	fw = 1346.62
a = 13.149 (5) Å	space group = $P\bar{1}$ (No. 2)
b = 13.662 (5) Å	T = 25 °C
c = 20.327 (5) Å	λ = 0.710 73
α = 92.36 (3)°	ρ_{calcd} = 1.37
β = 94.77 (3)°	μ = 4.73 cm⁻¹
γ = 115.46 (3)°	R = 0.0445
V = 3274.2 (2.1) Å³	dR_w = 0.0360
Z = 2	

the tetraselenometalates, even with highly crystalline, handpicked samples.

Preparation of [(C₆H₅)₄P]₂[MoSe₉]. A 0.18-g sample of [(C₆H₅)₄-P][MoSe₄] (0.16 mmol), prepared as described above, was combined with 0.06 g of gray selenium (0.80 mmol) in 10 mL of DMF. The mixture was stirred for 2 h at 25 °C, during which time the mixture turned deep red and all of the selenium disappeared. Upon filtration, addition of a 15-mL layer of THF, and storage at 4 °C overnight, deep red needles of [(C₆H₅)₄P]₂[MoSe₉] were produced (0.16 g; 65% yield). These crystals were suitable for structural analysis. Anal. Calcd for C₄₈H₄₀P₂MoSe₉: C, 38.79; H, 2.69. Found: C, 38.62; H, 2.78.

Preparation of [(C₆H₅)₄P]₂[WS₄]. A flask was charged with 0.15 g of K₂S₃ (0.86 mmol), 0.30 g of W(CO)₆ (0.85 mmol), and 0.72 g of (C₆H₅)₄PBr (1.72 mmol), and 10 mL of DMF was added. The mixture was stirred at 25 °C for 4 h, during which time the solution turned bright red. The solution was filtered and layered with 10 mL of THF, and this mixture was stored at low temperature as above. Red needles of product were obtained (0.40 g; 50% yield). Anal. Calcd for C₄₈H₄₀P₂WS₄: C, 58.18; H, 4.04. Found: C, 58.97; H, 3.85. UV/vis (DMF), λ_{max}: 399 nm.

Preparation of [(C₆H₅)₄P]₂[MoS₄]. A flask was charged with 0.16 g of K₂S₃ (0.72 mmol), 0.20 g of Mo(CO)₆ (0.76 mmol), and 0.60 g of (C₆H₅)₄PBr (1.43 mmol), and 10 mL of DMF was added. The resulting red solution was filtered and treated with 10 mL of THF, and this mixture was stored overnight at 4 °C as above. Bright red needles were obtained (0.37 g; 60% yield). Anal. Calcd for C₄₈H₄₀P₂MoS₄: C, 63.85; H, 4.43. Found: C, 62.86; H, 4.43. UV/vis (DMF), λ_{max}: 476 nm. Unit cell: space group $C2/c$, a = 10.891 Å, b = 19.236 Å, c = 19.856 Å, β = 91.180°, V = 4158 Å³.

Preparation of [(C₆H₅)₄P]₃[Cr(S₂CO)₃]. A flask was charged with 0.125 g of K₂S₃ (0.72 mmol), 0.16 g of Cr(CO)₆ (0.72 mmol), and 0.60 g of (C₆H₅)₄PBr (0.143 mmol). DMF (10 mL) was added, and the solution was stirred at 25 °C for 0.5 h. The resulting red solution was then heated at 90 °C for 1 h, during which time it turned dark blue. The solution was filtered and layered with 10 mL of THF, and this mixture was stored at 4 °C overnight. A white powder was deposited. This was removed by filtration, and fresh THF (3 mL) was added. Further storage at 4 °C overnight produced lustrous blue needle crystals suitable for X-ray diffraction study. Anal. Calcd for C₇₅H₆₀O₃CrP₃S₆: C, 66.91; H, 4.46. Found: C, 66.22; H, 4.52. IR (cm⁻¹): 1546(s), 1532(s), 876(m), 855(m). UV/vis (DMF), λ_{max}, nm (ϵ): 500 (460), 652 (484).

X-ray Crystallographic Studies. A dark blue needle of [(C₆H₅)₄P]₃-[Cr(S₂CO)₃] was placed in a glass capillary that was sealed in epoxy resin and mounted on a Nicolet R3 diffractometer. Preliminary and axial photographs provided crystal quality and unit cell information. The unit cell was determined from 40 well-centered reflections in the range 15° < 2θ < 30°. Application of several cell reduction programs did not reveal a higher symmetry unit cell. This and the lack of any systematic absences in the data confirmed the triclinic unit cell. Data were collected in the range 2° < 2θ < 45°, and the structure was solved by direct methods. It was refined in standard fashion using the SHELXTL package. All heavy atoms were refined anisotropically by using 6555 reflections with $F_o^2 > 3\sigma(F_o^2)$. All hydrogen atoms were fixed. Metrical information is provided in Table I. Absorption correction was performed via a ψ scan of six strong-intensity reflections.

Results

Reactions of Mo(CO)₆ and W(CO)₆ with Polysulfides and Polyselenides. The reaction of M(CO)₆ (M = Mo, W) with solutions of polyselenides or polysulfides leads to isolation of ME₄²⁻ in good yield. The structures of the selenides were confirmed by single-crystal X-ray diffraction,[11] and the sulfides are isomorphous with the selenides. Because the polychalcogen anions are in complex equilibrium in solution,[15] it difficult to write a balanced

equation for the reaction. The simplest possible equation is

$$M(CO)_6 + E_4^{2-} \rightarrow ME_4^{2-} + 6CO$$
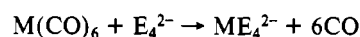
However, there is evidence that it is considerably more complex than that. The reactions with molybdenum carbonyl are faster than those with tungsten, in keeping with greater lability of second-row transition-metal complexes. The molybdenum reactions take place overnight at room temperature, whereas the tungsten reactions take a week of stirring to go to completion. Both reactions are complete within 1 h if the solutions are warmed to 90 °C under a static vacuum. The reaction involves a formal oxidation of the metal center from 0 to 6+. Presumably the chalcogens are reduced from a fractional oxidation state to 2− in the process.

Reactions with Cr(CO)₆. Unlike polytellurides, polyselenides do not produce a pure isolatable product upon reaction with Cr(CO)₆. IR spectroscopy indicates that a carbonyl anion is formed as an intermediate, but this could not be isolated. A red amorphous solid is isolated, which contains chromium and selenium but not carbonyls. Elemental analysis is not consistent but suggests a chromium to selenium ratio of about 1/5 or 1/6. Thus, we postulate that oxidative decarbonylation takes place, producing a mixture of chromium selenides such as Cr₂Se₁₀²⁻ or Cr₂Se₁₂²⁻. However, the products have resisted all attempts at crystallization, despite varying solvent, counterion, and conditions. Use of other carbonyl reagents such as Cr(CO)₃(CH₃CN)₃ or Cr(CO)₃-(mesitylene) has also been uniformly unsuccessful. The red solution also reacts with red selenium to form an unstable product, which deposits selenium upon standing.

In contrast, the reaction of Cr(CO)₆ with polysulfide solution is quite unusual. It generates the tris(dithiocarbonate) complex Cr(S₂CO)₃³⁻ in good yield. It should be noted that this again involves an oxidation of the metal center, in this case to Cr³⁺. Presumably, the polysulfide is not capable of oxidizing chromium to the 6+ state but instead oxidizes carbon from 2+ to 4+. Though we are still in the process of investigating the other metal carbonyls with polychalcogenides, we have found no evidence of diseleno- or dithiocarbonate formation in other systems. We are unable to offer an explanation for the occurrence of this product.

There have been several dithiocarbonate complexes reported previously,[16] but in general they are rare because of the tendency of the parent ligand to disproportionate. Most of the complexes have been obtained by reaction of a coordinated ligand such as a xanthate or a phosphine adduct of carbon disulfide,[17] although several have been prepared by direct reaction. However, they are much less common than the isoelectronic xanthates and dithiocarbamates.

The IR spectrum of [Cr(S₂CO)₃]³⁻ is distinctive and deserves comment. It contains strong bands at 1546, 1532, 876 and 855 cm⁻¹. The higher wavenumber stretches can be assigned to a symmetric and an asymmetric stretch of the carbonyls, as discussed previously.[18] However, other dithiocarbonate complexes have CO stretches above 1600 cm⁻¹, so our values are somewhat lower. We attribute this to the high overall charge density on the chromium complex. Previous workers only observed one low-frequency stretch assigned to C–S stretching. However, we observe at least two bands, one which is probably split further (see Figure 1). We attribute this to the unsymmetrical coordination environment around the metal atom (vide infra).

Structure of [(C₆H₅)₄P]₃[Cr(S₂CO)₃]. The structure of the dithiocarbonate has been determined by single-crystal X-ray diffraction studies (see Table I). It consists of three well-separated tetraphenylphosphonium cations and three dithiocarbonate ligands

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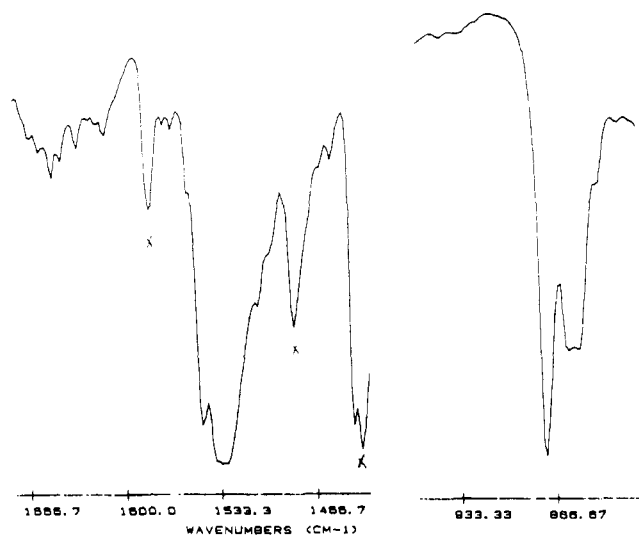
Figure 1. IR spectrum of a Nujol mull of $[Cr(S_2CO)_3]^{3-}$, showing detail of bands near 1500 and 800 cm^{-1} attributed to C=O and C–S stretches, respectively. (Peaks marked with an X are due to Nujol oil or $(C_6H_5)P^+$.)
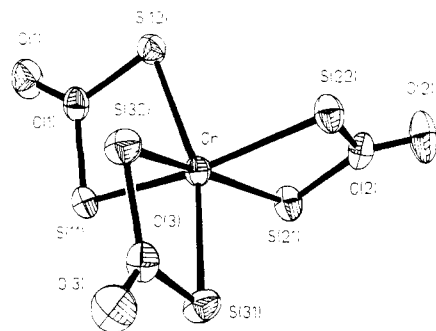

Figure 2. ORTEP drawing of $[Cr(S_2CO)_3]^{3-}$ with thermal ellipsoids at 40% probability level. This view shows the distorted octahedral coordination environment around chromium.

chelated through sulfur atoms to a chromium(III) atom (see Figure 2). The parameters in our compound are similar to those observed previously[17,19] (see Table II). The Cr–S bond lengths average 2.41 Å, which is comparable to other chromium–sulfide distances (2.40 Å in $[(NH_3)_2Cr(S_5)_2]^-$).[20] The C—S bond lengths average 1.75 Å, and the C=O bond length is quite short at 1.22 Å. The C=O distances vary somewhat in known dithiocarbonates, ranging from 1.195 Å in $Pt(S_2CO)(PPh_3)_2$[19b] to 1.27 Å in $[(triphos)Co(S_2CO)]$.[17] This variation has been attributed to the difference in π-electron-withdrawing effects of the metal and other ligands.[19b] The S–C–S angles are about 110°, and this is also typical for this ligand. However, the small angle decreases the bite angle of the ligand and causes Cr(III) to be in a distorted octahedral geometry. Thus, the S–Cr–S angle for trans sulfur atoms is 163° and is 73° for cis sulfur atoms on the same carbon versus 95° for the others.

It is well-known that coordinated dithiocarbonates react readily with electrophiles such as metal cations[20] or with light,[21] resulting in rapid loss of CO and formation of metal sulfides. Similarly, the tris(dithiocarbonate) complex reacts instantly with elemental sulfur in DMF solution. All the dithiocarbonate bands disappear from the IR spectrum, and a binary sulfide anion is presumably formed. However, like the binary chromium selenide, it has defied

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Table II. Bond Lengths (Å) and Bond Angles (deg) for $[(C_6H_5)_4P]_3[Cr(S_2CO)_3]$

Bond Lengths			
Cr–S(11)	2.409 (1)	Cr–S(12)	2.421 (1)
Cr–S(21)	2.421 (1)	Cr–S(22)	2.399 (1)
Cr–S(31)	2.401 (1)	Cr–S(32)	2.407 (1)
S(11)–C(1)	1.758 (4)	S(12)–C(1)	1.751 (4)
S(21)–C(2)	1.738 (5)	S(22)–C(2)	1.746 (4)
S(31)–C(3)	1.749 (4)	S(32)–C(3)	1.750 (4)
O(1)–C(1)	1.221 (4)	O(2)–C(2)	1.215 (5)
O(3)–C(3)	1.225 (4)		

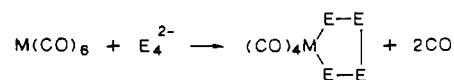| Bond Angles			
S(12)–Cr–S(11)	73.3 (1)	S(21)–Cr–S(11)	96.8 (1)
S(21)–Cr–S(12)	97.8 (1)	S(22)–Cr–S(11)	163.5 (1)
S(22)–Cr–S(12)	94.9 (1)	S(22)–Cr–S(21)	72.9 (1)
S(31)–Cr–S–(11)	94.6 (1)	S(31)–Cr–S(12)	162.1 (1)
S(31)–Cr–S(21)	96.6 (1)	S(31)–Cr–S(22)	99.4 (1)
S(32)–Cr–S(11)	96.9 (1)	S(32)–Cr–S(12)	94.4 (1)
S(32)–Cr–S(21)	163.7 (1)	S(32)–Cr–S(22)	95.5 (1)
S(32)–Cr–S(31)	73.6 (1)	C(1)–S(11)–Cr	88.0 (1)
C(1)–S(12)–Cr	87.8 (1)	C(2)–S(12)–Cr	87.9 (1)
C(2)–S(22)–Cr	88.3 (2)	C(3)–S(31)–Cr	87.9 (1)
C(3)–S(32)–Cr	87.7 (1)	S(12)–C(1)–S(11)	110.6 (2)
O(1)–C(1)–S(11)	124.2 (3)	O(1)–C(1)–S(12)	125.2 (3)
S(22)–C(2)–S(21)	110.6 (2)	O(2)–C(2)–S(21)	125.0 (4)
O(2)–C(2)–S(22)	124.3 (4)	S(32)–C(3)–S(31)	110.8 (2)
O(3)–C(3)–S(31)	124.2 (3)	O(3)–C(3)–S(32)	125.0 (3)
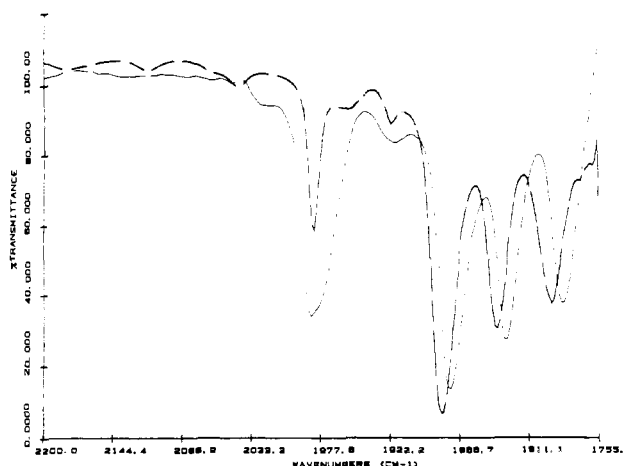
Figure 3. IR spectrum of a DMF solution containing $[Cr(CO)_4Te_4]^{2-}$ (dashed line) superimposed on an IR spectrum of a DMF solution containing $Mo(CO)_6$ and polyselenides (solid line).

all attempts at crystallization in our hands. We are currently exploring extensions of this reaction.

Discussion

The reaction of molybdenum and tungsten carbonyls with polyselenides and polysulfides unexpectedly leads to oxidation of the metal center to its maximum oxidation state with loss of all carbonyls. It is known that solutions of polychalcogen anions contain an equilibrium mixture of chains of different lengths. These chains obviously undergo a series of complex internal redox reactions while coordinated to the low-valent metal centers inducing the oxidative decarbonylation.
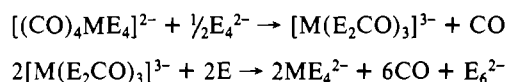
Careful IR studies of the reaction mixture soon after addition of polychalcogen anions show a carbonyl stretching pattern almost superimposable on that of the previously characterized $[(CO)_4MTe_4]^{2-}$ complexes[12] (see Figure 3). Thus, we propose an initial step in the oxidative decarbonylation reaction as follows:

$$M(CO)_6 + E_4^{2-} \longrightarrow (CO)_4M \overset{E—E}{\underset{E—E}{|}} + 2CO$$

All attempts to isolate any of these intermediates, either through quenching or low-temperature crystallization, have failed. Only the final ME_4^{2-} products are obtained. In contrast, the polytelluride complexes are extremely thermally stable. They can be

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]

$$Re_2(CO)_{10} + Se_n^{2-} \rightarrow [Re_2(Se_4)_2(CO)_6]^{2-}$$
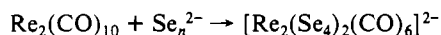
The facile reaction of coordinated dithiocarbonate with elemental sulfur prompts speculation that it may be an intermediate in the oxidative decarbonylation reaction observed with molybdenum and tungsten as well. Thus, rearrangement of the coordinated polychalcogen could form dichalcogenocarbonate. Rapid reaction of this with elemental chalcogen could lead to the observed products and higher order polychalcogens, which are well-known.[24]

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(24) Teller, R. G.; Krause, L.; Haushalter, R. C. *Inorg. Chem.* **1983,** *22,* 1809.

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.

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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Synthesis and Coordination Properties of (Sulfinylmethyl)phosphonates and (Sulfonylmethyl)phosphonates. Crystal and Molecular Structure Determinations for UO2(NO3)2[(i-C3H7O)2P(O)CH2S(O)2C6H11]2 and Gd(NO3)3[(i-C3H7O)2P(O)CH2S(O)(p-CH3C6H4)]·H2O

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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: $U\text{-}O(\text{uranyl})_{av} = 1.763\ (8)$ Å, $U\text{-}OP(1) = 2.325\ (9)$ Å, and $U\text{-}OP(2) = 2.489\ (9)$ 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 $Gd\text{-}O(P) = 2.319\ (4)$ Å and $Gd\text{-}O(S) = 2.340\ (5)$ Å, and a water oxygen atom with $Gd\text{-}OH_2 = 2.378\ (5)$ 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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