Phe NH resonance is plotted in Figure 2, with the transient NOE for comparison. A 5-kHz field centered on the NH resonance has been used. The MP sequences give a somewhat slower buildup than continuous irradiation, in agreement with eqs 1 and 5.

The suppression of TOCSY in T-ROESY experiments is an important advance. In the two-dimensional version of the experiment, absorption-mode line shapes can be achieved along the lines of ref 15.

Acknowledgment. This material is based upon work supported by the National Science Foundation (CHE-8957560). Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We have profited from discussions with Mr. Gavin Estcourt and Dr. James Keeler of Cambridge University.

Synthesis of Lanthanide(II) Complexes of Aryl Chalcogenolate Ligands: Potential Precursors to Magnetic Semiconductors

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Received September 19, 1991

The synthesis of molecular precursors to semiconducting II–VI materials has attracted considerable attention since these materials are technologically important as optical materials and often difficult to synthesize by conventional methods.[2,3] Among these are a class known as the diluted magnetic semiconductors, which are ternary alloys of conventional II–VI materials, such as HgTe, substituted with paramagnetic centers such as Mn^{2+} or Fe^{2+}. These materials have a wide range of potential magnetooptic applications.[3] The rare earth monochalcogenides LnQ (Ln = Yb, Eu, Sm; Q = S, Se, Te) are of interest in this area due to the great variety of dilute magnetic semiconductors they could be used to form, such as $Hg_{1-x}Sm_xTe$, as well as for their range of magnetic properties.[4] Conventional high-temperature syntheses of these materials, particularly those containing the heavier chalcogenides, are difficult and often hindered by impurities incorporated due to the high oxophilicity of the rare earth centers.[5] The synthesis of precursor complexes to rare earth monochalcogenides, with the elements combined on a molecular level in the correct stoichiometry, allows for purification before pyrolytic cleavage and might afford the ability to process these materials at much lower temperatures. Reported complexes of the lanthanide metals with heavier chalcogenide ligands (Se, Te) are very few, but some examples exist of stable compounds of trivalent lanthanide ions coordinated by selenium and tellurium-containing ligands,[6] though divalent analogues have not been reported previously. We report here the synthesis of several members of a new class of compounds, lower chalcogenide complexes of the divalent lanthanide metals, which we find to be promising precursors to rare earth monochalcogenides.

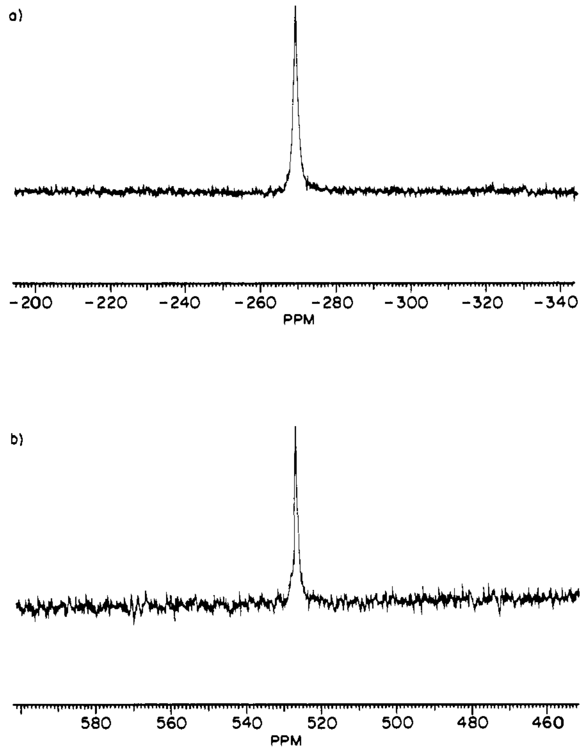

Figure 1. (a) ^{125}Te NMR spectrum of $Yb(TeMes)_2THF_{2-3}$ (**1**) in d_8-THF, referenced to external Me_2Te (δ = 0 ppm).[17] Resonance observed after 10 200 scans with sweep width = 100 000 MHz, pulse width = 3.0 μs, and relaxation delay = 0.1 s. (b) ^{171}Yb NMR spectrum of **1** referenced to external $YbCp_2{}^*THF_2$ (δ = 0 ppm).[18] Resonance observed after 2030 scans with the same parameters as above but a relaxation delay of 1.6 s.

Our most successful synthesis involves metathesis of halide ligands on divalent lanthanide metals[7] with alkali-metal salts of aryl selenolates or tellurolates (eq 1). Ytterbium was the metal

$$\mathrm{LnX_2THF_{2-3}} + 2\mathrm{KQMes} \xrightarrow[\mathrm{DME}]{\mathrm{THF}} \mathrm{Ln(QMes)_2THF_{2-3}} + 2\mathrm{KX} \tag{1}$$

Ln = Yb, Sm, Eu; X = I, Br; Q = Se, Te; Mes = 2,4,6-trimethylphenyl

selected for initial study because of its diamagnetism in the +2 oxidation state, allowing characterization by multinuclear NMR spectroscopy, and oxidation state confirmation by magnetic measurements. The lanthanide elements exhibit similar chemistry, allowing complexes analogous to the characterized ytterbium models to be synthesized with samarium and europium.

To produce stable complexes, the organic group on the chalcogenide must be bulky in order to sterically saturate the divalent lanthanide ion and maintain a monomeric or low nuclearity structure, allowing solubility in organic solvents and blocking possible decomposition pathways.[9] Syntheses of analogous

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[8] Spectral data for $Yb(TeMes)_2THF_{2-3}$ (**1**): ^{1}H NMR (d_8-THF, 300 MHz) δ 6.62 (s, 4 H), 3.58 (THF), 2.42 (s, 12 H), 2.04 (s, 6 H), 1.73 ppm (THF); $^{13}C\{^1H\}$ NMR δ 145.4, 132.1, 125.5, 117.9 (aromatics), 68.2 (THF), 33.4 (o-CH_3), 26.3 (THF), 20.8 (p-CH_3). Anal. Calcd for $YbTe_2C_{28}H_{42}O_{2.5}$ (2.5 coordinated THF): Yb, 20.4; Te, 30.1; C, 39.7; H, 5.0. Found: Yb, 20.5; Te, 29.8; C, 39.2; H, 5.1.

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complexes using phenyl substituents on the tellurolate gave, as soluble products, lanthanide complexes which retained alkali-metal halide salts. In addition, insoluble materials often formed which probably consist of higher order clusters, oligomers, or polymers.[2c,10] The use of 2,4,6-trisubstituted aryl substituents enabled isolation of soluble complexes (eq 1). The potassium salts of the aryl tellurolates react much more cleanly than do the analogous lithium salts because lithium halides tend to coordinate to the lanthanide products more readily, a feature commonly observed in organolanthanide chemistry.[11] The potassium salt of mesityl tellurolate can be prepared by the metathesis reaction of LiTeMes[12] with potassium *tert*-butoxide or by the recently reported reduction of the ditelluride[13] with potassium tris(*sec*-butyl)borohydride.[14] Solvent-free KTeMes can be isolated by drying under vacuum.[15]

The ytterbium(II) complex of this ligand is extremely air-sensitive and soluble in toluene, dimethoxyethane, and THF. The complex is crystallized in 85% yield from a cooled solution of toluene and THF as orange crystals and is found to be diamagnetic by magnetic susceptibility measurements made on a Gouy balance, becoming paramagnetic upon exposure to air. Elemental analysis confirmed that both tellurolate ligands substituted onto the complex, for a Yb:Te ratio of 1:2, with no halogens detected, was obtained.[8]

The complex was further characterized by ^{125}Te and ^{171}Yb NMR.[16] The ^{125}Te spectrum, in d_8-THF (Figure 1a), showed a single resonance at −270 ppm, shifted 26 ppm downfield from the resonance of KTeMes. The ^{171}Yb nucleus has a single resonance, which can be observed (Figure 1b) at +526 ppm. Both resonances are somewhat broad ($\Delta w_{1/2}$ = 60–125 Hz), possibly due, in the ^{125}Te case, to unresolved coupling to ytterbium [^{173}Yb nucleus (16% abundant, $I = {}^5/_2$) and ^{171}Yb nucleus (14% abundant, $I = {}^1/_2$)] or to rapid ligand or solvent exchange occurring in solution at room temperature. Low-temperature NMR studies on the diglyme adduct of this Yb(II) complex show that solvent exchange may be occurring, but no ligand exchange via tellurolates bridging to form dimer or cluster species[2b,18] is evident even at −60 °C. The simplicity of all the NMR spectra,[8] as well as the lack of tellurolate ligand exchange seen at low temperature, suggests a monomeric structure for these complexes.

Complexes can be similarly synthesized using Sm(II) and Eu(II), which are paramagnetic in the divalent state, as well as complexes of analogous selenolate ligands.[19] The complex Sm(TeMes)$_2$THF$_2$ (**2**) is isolated in approximately 67% yield as dark green crystals.[20] Elemental analysis confirms the formulation of complete substitution of the halide anions by the tellurolate ligands. These samarium tellurolate and selenolate compounds have magnetic moments of approximately 3.1 μ_B, consistent with Sm(II).[21] The selenolate complexes can be prepared but are not as soluble as the tellurolate congeners.[19]

Preliminary results on the thermal decomposition of these divalent lanthanide complexes suggest that they possess the correct stoichiometry to act as precursors to rare earth monochalcogenides. Pyrolysis of the Yb(II) complex occurs in refluxing toluene or at 250–300 °C in vacuo to produce a black insoluble char[22a] and releases volatile organotelluride byproducts. The byproducts, studied by ^{125}Te NMR, display a resonance at +253 ppm in d_6-benzene corresponding to dimesityl monotelluride (TeMes$_2$).[13] The formation of TeMes$_2$ as the major pyrolysis byproduct is expected upon deposition of LnTe from these divalent complexes (eq 2), and analogous species have been observed in the pyrolytic decomposition of precursors to other metal chalcogenides.[2a] Annealing the char obtained from low-temperature pyrolysis of **1** at 900 °C for 24 h under argon yields a crystalline powder containing YbTe as seen by its X-ray powder diffraction pattern.[22b] These data suggest that decomposition to lanthanide tellurides is proceeding at low temperatures.

$$\mathrm{Ln(TeMes)_2THF_{2-3}} \xrightarrow{\Delta} \mathrm{LnTe} + \mathrm{TeMes_2} \qquad (2)$$

This method utilizing molecular precursors and milder reaction conditions appears promising in the preparation of rare earth monochalcogenides. It affords the advantages of purification of the soluble precursors by conventional organometallic techniques prior to thermal decomposition and an oxygen-free, lower-temperature pyrolysis. The synthesis of the precursor complexes, the first divalent lanthanide complexes of the lower chalcogenide ligands, adds a new class of compounds to those known for lanthanides in this lower oxidation state. Further studies utilizing higher temperatures following deposition of rare earth monochalcogenides to determine crystallinity of the phases obtained from these organometallic precursors are continuing.

Acknowledgment. We thank Dr. Alan Benesi of Pennsylvania State University for his advice in obtaining multinuclear NMR spectra. A.R.S thanks the Shell Oil Foundation for a graduate fellowship. We also thank Dr. M. Steigerwald for helpful and informative discussions.

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(20) Spectral data for Sm(TeMes)$_2$THF$_2$ (**2**): ^{1}H NMR (d$_8$-THF, 300 MHz) δ 7.51 (s, 4 H), 4.45 (s, 12 H), 3.61 (br, THF), 1.76 (br, THF), 1.46 (s, 6 H); ^{13}C{^{1}H} NMR δ 132.9, 130.0, 120.9 (aromatics, ipso carbon missing), 68.4 (THF), 41.4 (*o*-CH$_3$), 22.5 (THF), 21.5 ppm (*p*-CH$_3$). Anal. Calcd for SmTe$_2$C$_{26}$H$_{38}$O$_2$: Sm, 19.1; Te, 32.4; C, 39.6; H, 4.9. Found: Sm, 19.1; Te, 31.8; C, 40.2; H, 4.9.

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New Evidence Supporting a Radical Mechanism of the Inactivation of General Acyl-CoA Dehydrogenase by a Metabolite of Hypoglycin

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Received December 20, 1991

General acyl-CoA dehydrogenase (GAD) is a FAD-dependent enzyme which catalyzes the conversion of a medium-chain fatty acyl-CoA to the corresponding α,β-enolyl-CoA product.[1] When GAD is exposed to (methylenecyclopropyl)acetyl-CoA (MCPA-CoA, **1**), a metabolite of hypoglycin A that causes Jamaican vomiting sickness,[2] time-dependent inactivation ensues with concomitant bleaching of the active-site FAD.[3] This inhibition

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