# COMMUNICATION

## LOW TEMPERATURE ROUTES TO EUROPIUM AND YTTERBIUM CHALCOGENIDES

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Abstract—Reaction of europium or ytterbium metal in liquid ammonia with sulphur, selenium or tellurium (at room temperature in a pressure tube) affords a convenient route to crystalline binary metal chalcogenides.

The solubility of alkali metals and alkaline metal earths in ammonia to generate blue or bronze solutions containing solvated electrons and metal cations is well known.<sup>1</sup> These solutions have been used to perform a range of reductions both in organic chemistry in, for instance, the Birch reduction<sup>2</sup> and in inorganic chemistry to afford metal polychalcogenide species,  $M_x E_y$  (M = group Ia, IIa; E = chalcogenide,  $y \ge x$ ).<sup>3</sup> Europium and to a lesser extent ytterbium metal also dissolve in liquid ammonia to form deep blue or bronze solutions;<sup>4</sup> however, the synthetic utility of these solutions (to our knowledge) has not been reported.

Lanthanide sulphides, selenides and tellurides of varying stoichiometry LnE to  $Ln_3E_7$  (E = S, Se, Te; Ln = lanthanide) have been synthesized by high temperature (> 1000°C) techniques, either by reduction of the metal oxide with H<sub>2</sub>S and H<sub>2</sub>Se or by direct combination of the elements.<sup>5</sup> Here we report the room temperature synthesis of crystalline europium and ytterbium chalcogenides.

### **RESULTS AND DISCUSSION**

Reaction of europium metal in liquid ammonia at room temperature in a pressure tube with sulphur, selenium or tellurium affords the binary compounds EuE (E = S, Se, Te) (Table 1). The europium and chalcogenide were added under nitrogen to ammonia at  $-77^{\circ}$ C to generate a deep blue or bronze solution, which was magnetically stirred and allowed to warm to room temperature (under pressure). The ammonia was maintained in the system by closing a Young's tap; after a couple of hours the blue or bronze colour was discharged and a green, yellow or purple homogeneous precipitate formed dependent on the ratio of europium to chalcogenide. After 12 h the solution was cooled and the ammonia allowed to evaporate under nitrogen. Removal of the final traces of ammonia in vacuo generally darkened the precipitate to black in the case of tellurium and dark red-brown for the selenium or sulphur derivatives. The reaction of excess europium with the chalcogenides leads to the formation of a pyrophoric material comprising of finely divided metal and metal chalcogenide. Reaction of excess chalcogenide with europium leads to the formation of the same metal species (Table 1) and unreacted chalcogenide, as detected both by X-ray powder diffraction and by extraction of the chalcogenide with CS<sub>2</sub>.

The precipitates were characterized by microanalysis, S.E.M./EDAX, X-ray powder diffraction, magnetic moment measurement and IR spectroscopy. The IR spectra† showed only a broad band at 400 cm<sup>-1</sup> for EuS with no evidence of any S—H or N—H stretches. The microanalysis of EuE showed no carbon, hydrogen or nitrogen present and chalcogenide analyses were satisfactory.

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<sup>&</sup>lt;sup>†</sup> Measurements obtained by KBr pressed pellets on a Nicolet (CsI)205 spectrometer.

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Table 1. Crystalline phases detected by X-ray powder pattern from evaporation of ammonia from reaction of europium or ytterbium with a chalcogen in liquid ammonia

Metal	Chalcogenide			
	0	S	Se	Те
Europium Ytterbium	$\frac{\mathrm{Eu}_{2}\mathrm{O}_{3}{}^{a}}{\mathrm{Yb}_{2}\mathrm{O}_{3}{}^{a}}$	EuS/Eu <sub>3</sub> S <sub>4</sub> YbS/Yb <sub>3</sub> S <sub>4</sub>	EuSe YbSe <sup>b</sup>	EuTe YbTe <sup>b</sup>

<sup>a</sup>Oxide formed by exposing the finely divided metal to air. **Caution:** extremely exothermic reaction.

<sup>b</sup> Material heated in the pressure tube to  $250^{\circ}$ C for 2 h after NH<sub>3</sub> evaporated.



Fig. 1. S.E.M./EDAX elemental profile of europium selenide, EuSe.

The S.E.M./EDAX analysis\* showed both a homogenous morphology and elemental profile standardized as EuE (Fig. 1). Samples of EuE decompose slowly in air, liberating  $H_2E$  and the formation of  $Eu_2O_3$ . Incorporation of oxygen was shown by a small peak in the EDAX analysis which increased in size with sample age.

The magnetic moments<sup>†</sup> and colours of the EuE compounds were identical to the literature.<sup>5</sup>

The X-ray powder diffraction data<sup>‡</sup> showed that the product from the room temperature reaction was crystalline, with the predominant phase being EuE (Fig. 2). In the case of excess sulphur to europium a small amount of  $Eu_3S_4$  and sulphur was also detected. When the reaction of selenium and tellurium with europium was performed with up to an eight-fold excess of the chalcogenide only EuSe and selenium metal or EuTe and tellurium metal were detected.

The analogous reactions with ytterbium were investigated. These showed that with selenium and tellurium even in excess only a small amount of YbSe and YbTe was formed after evaporation of the ammonia. The majority of material present was in the form of unreacted and finely divided metal. On exposure to air this powder ignited and pro-

<sup>\*</sup> S.E.M. were obtained on a JEOL 820i with EDAX using a Kevex program.

<sup>†</sup> Magnetic moments were determined via the Evans method on a Johnson-Matthey balance.

<sup>&</sup>lt;sup>‡</sup>X-ray powder diffraction data were obtained on a Siemens diffractometer D5000.



Fig. 2. X-ray powder diffraction pattern from reaction of europium with selenium in liquid ammonia at room temperature.

duced the metal oxide  $Yb_2O_3$ . However, YbSe and YbTe can be formed by gentle thermolysis of the ammonia precipitate (fully intermixed ytterbium and selenium or tellurium) at 250°C for 2 h under vacuum. Ytterbium sulphide formed at room temperature under the same conditions as the europium analogue.

Convenient preparation of both  $Eu_2O_3$  and  $Yb_2O_3$  can be achieved by generating finely divided metal by adding europium or ytterbium metal to liquid ammonia and allowing the ammonia to evaporate with vigorous stirring; careful pouring of the metal powder onto a ceramic dish (in air) causes spontaneous ignition and formation of the metal oxide.

, The formation of europium and ytterbium chalcogenide by the ammonia route is significantly lower in energy than that of previous studies, where elevated temperatures were required.<sup>5</sup> However, it does seem limited to europium and ytterbium, as the other lanthanides are not soluble in ammonia. Indeed reaction of samarium and gadolinium under the same conditions failed to generate metal chalcogenides.

The chalcogenides are soluble in ammonia, forming a variety of different ions dependent on the concentration of the chalcogenide.<sup>6</sup> The reactions described here seem to proceed analogously to group IA and IIa chemistry where  $M_2E$  and ME compounds are known,<sup>7</sup> however, with excess chalcogenide no lanthanide polychalcogenide species are produced.

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