

According to Gschneidner and Valletta<sup>8</sup> if the pressure required for synthesis increases with the atomic number of the rare earth, there must be 4f-electron participation in the chemical bonding. If it decreases with increasing atomic number, there is no 4f bonding and crystal structure is determined by size effects only. It appears that in this system both the size effect and 4f bonding are important for GdSb<sub>2</sub>, TbSb<sub>2</sub>, and DySb<sub>2</sub>, but 4f bonding becomes increasingly important for the heavier rare earths.

The diantimonide of yttrium required about 10 kbars higher pressure for synthesis than would be predicted by its ionic radius. This same effect has been observed in other yttrium systems.<sup>8,9</sup> There are, of course, no 4f electrons in yttrium.

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(8) K. A. Gschneidner, Jr., and R. M. Valletta, *Acta Met.*, **16**, 477 (1968).

(9) A. W. Webb, Ph.D. Dissertation, Brigham Young University, May 1969.

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### High-Pressure Th<sub>3</sub>P<sub>4</sub>-Type Polymorphs of Rare Earth Sesquiselenides

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Previous work has shown that the normal monoclinic and rhombohedral forms of rare earth sesquisulfides could be converted to the more dense Th<sub>3</sub>P<sub>4</sub>-type cubic structure by high-pressure-high-temperature techniques.<sup>2</sup> Also, the Th<sub>3</sub>P<sub>4</sub> forms of Ho<sub>2</sub>Se<sub>3</sub> and Er<sub>2</sub>Se<sub>3</sub> have been synthesized from the elements using high-pressure techniques.<sup>2</sup> We have now succeeded in preparing Tm<sub>2</sub>Se<sub>3</sub>, Yb<sub>2</sub>Se<sub>3</sub>, Lu<sub>2</sub>Se<sub>3</sub>, and Y<sub>2</sub>Se<sub>3</sub> in the Th<sub>3</sub>P<sub>4</sub>-type structure by applying high pressure-high temperature to a stoichiometric mixture of the elements. Consequently, all the rare earth sesquiselenides except Eu<sub>2</sub>Se<sub>3</sub> are now known in the Th<sub>3</sub>P<sub>4</sub> structure.

#### Experimental Section

The studies were carried out in a tetrahedral press with 0.5-in. anvils equipped with an anvil guide.<sup>3,4</sup> Sample geometry and experimental procedure were the same as described previously.<sup>2</sup> Pressures above 70 kbars were calibrated by taking the Bi(III)-Bi(IV) transition pressure to be 77 kbars.

#### Results and Discussion

The Th<sub>3</sub>P<sub>4</sub>-type polymorphs of Y<sub>2</sub>Se<sub>3</sub>, Tm<sub>2</sub>Se<sub>3</sub>, Yb<sub>2</sub>Se<sub>3</sub>, and Lu<sub>2</sub>Se<sub>3</sub> have been synthesized from stoichiometric mixtures of the elements using the conditions

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(2) N. L. Eatough, A. W. Webb, and H. T. Hall, *Inorg. Chem.*, **8**, 2069 (1969).  
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(4) H. T. Hall, *ibid.*, **33**, 1278 (1962).

TABLE I

CUBIC RARE EARTH SESQUISELENIDES

	Pressure, kbars	Temp, °C	Lattice parameter, Å
Y <sub>2</sub> Se <sub>3</sub>	70	1800	8.6626 ± 0.0008
Tm <sub>2</sub> Se <sub>3</sub>	70	1800	8.5992 ± 0.0007
Yb <sub>2</sub> Se <sub>3</sub>	80	1800	8.615 ± 0.002
Lu <sub>2</sub> Se <sub>3</sub>	90	1800	8.570 ± 0.003

indicated in Table I. No extraneous lines were observed in the X-ray diffraction patterns of the products, showing that the polymorphs were single phase. For runs at temperatures or pressures less than those given in Table I the diselenide was obtained as the major product.

Guittard, *et al.*,<sup>5</sup> found the sesquiselenide series from Gd<sub>2</sub>Se<sub>3</sub> to Dy<sub>2</sub>Se<sub>3</sub> to be nonstoichiometric with a selenium deficiency. It is quite possible that the cubic polymorphs made in this work are also nonstoichiometric; however, facilities were not available to handle the small samples prepared so no chemical analysis of the compounds formed was made.

Lattice parameters of the new cubic sesquiselenides are compared with previously known compounds of this type in Figure 1.<sup>2,6</sup> It can be seen that Y<sub>2</sub>Se<sub>3</sub> fits well

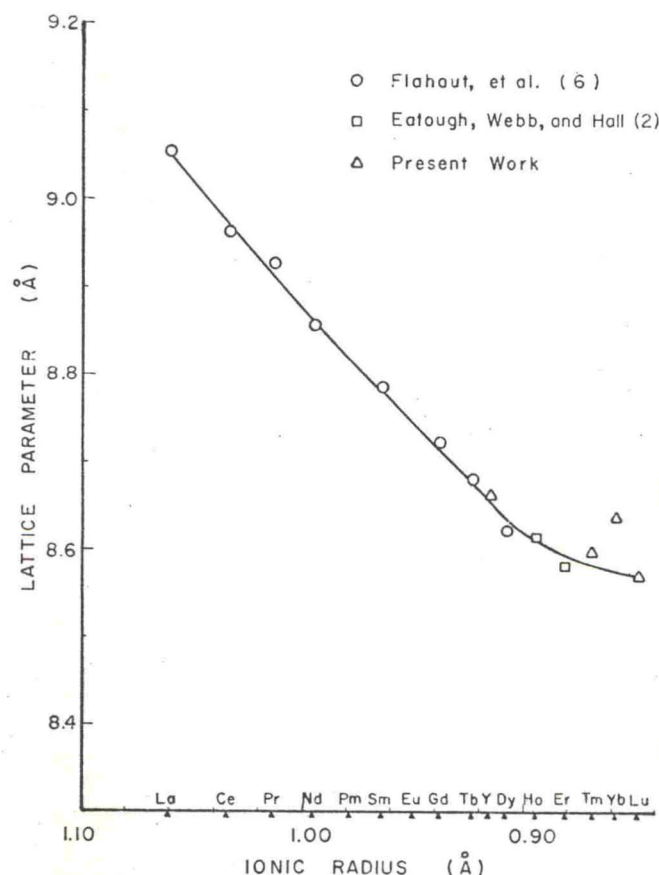


Figure 1.—Variation of lattice parameter with ionic radius of the Th<sub>3</sub>P<sub>4</sub>-type rare earth sesquiselenides.

at an ionic radius of 0.915 Å which is the same value as previously obtained for the sesquisulfide.<sup>2</sup> Ionic radii for the other rare earths were taken from Templeton and

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Dauben.<sup>7</sup> The lattice parameters of  $\text{Tm}_2\text{Se}_3$  and  $\text{Lu}_2\text{Se}_3$  are somewhat larger than would be predicted from a straight-line extrapolation of the lighter rare earths, and this same effect has been previously observed for the sesquisulfides. The lattice parameter of  $\text{Yb}_2\text{Se}_3$  is somewhat greater than its neighbors which indicates some  $\text{Yb}^{2+}$  character in  $\text{Yb}_2\text{Se}_3$ . This same effect was also observed in  $\text{Yb}_2\text{S}_3$ .<sup>2</sup> A graph of the minimum pressure for synthesis of the cubic polymorphs as a function of ionic radius of the rare earth is shown in Figure 2. Values for  $\text{Ho}_2\text{Se}_3$  and  $\text{Er}_2\text{Se}_3$  were

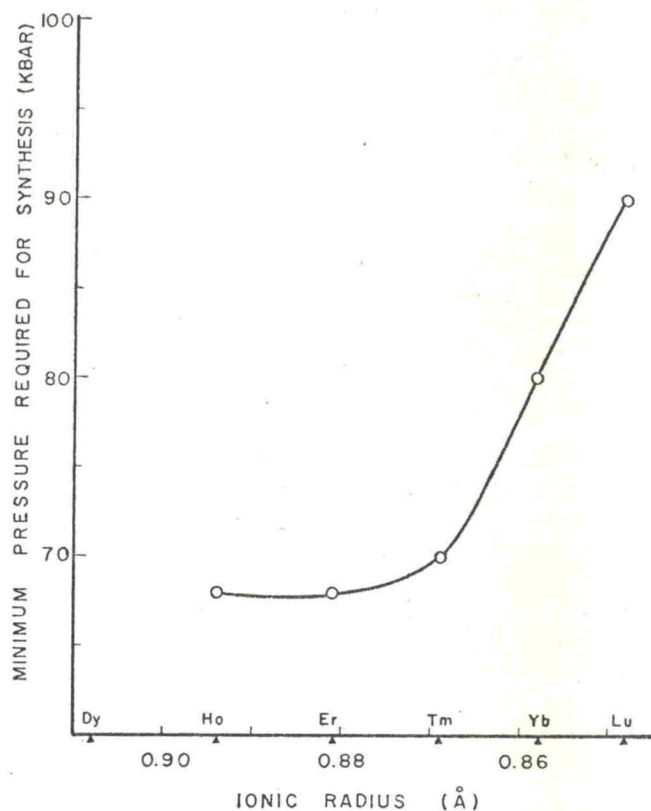


Figure 2.—Minimum pressure required for synthesis of cubic rare earth sesquiselenides.

taken from Eatough, Webb, and Hall.<sup>2</sup> The synthesis of  $\text{Ho}_2\text{Se}_3$ ,  $\text{Er}_2\text{Se}_3$ , and  $\text{Tm}_2\text{Se}_3$  takes place at about the same pressure. According to Gschneidner and Valletta<sup>8</sup> if the pressure required for synthesis increases with atomic number of the rare earth, there is 4f-electron participation in the chemical bonding. If the pressure required decreases with increasing atomic number, the crystal structure of the compound is determined by size effects only. In the sesquiselenide series there seems to be a combination of size effect and 4f-electron bonding determining the structure for the cubic polymorphs of Ho, Er, and Tm. For Yb and Lu the 4f bonding becomes increasingly important.

**Acknowledgments.**—Thanks are extended to the Army Research Office (Durham) for financial support during this research.

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(8) K. A. Gschneidner, Jr., and R. M. Valletta, *Acta Met.*, **16**, 477 (1968).

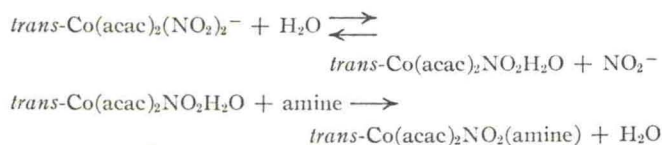
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### Stereochemistry of $\beta$ -Diketone Complexes of Cobalt(III). III. *cis* and *trans* Isomers of Nitroaminebis(acetylacetonato)cobalt(III)<sup>1</sup>

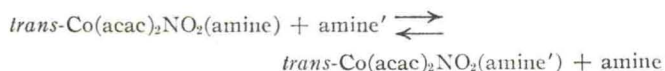
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The reaction of the anion<sup>2</sup>  $\text{trans-Co}(\text{acac})_2(\text{NO}_2)_2^-$  with a variety of amines leads rapidly to the exclusive formation of a *trans* product *via* the scheme<sup>3-5</sup>



The above reactions appear to be an example of the octahedral *trans* effect of the nitro ligand. Although a previous study<sup>3</sup> did not report an amine-exchange reaction, more careful work reveals that this reaction does occur rapidly at elevated temperatures as<sup>6</sup>



Thus the nitro ligand exerts a general rather than a specific *trans* effect in these complexes. In the course of studying the kinetics of amine-exchange reactions, we have observed the formation of several new complexes. We wish to report here the preparation and characterization of the previously unknown *cis* isomers of the amine complexes with the two representative amines pyridine and 4-*t*-butylpyridine.

#### Experimental Section

**Synthesis of Complexes.**— $\text{Na}[\text{trans-Co}(\text{acac})_2(\text{NO}_2)_2]$  was prepared as previously described.<sup>1</sup> Reagent grade pyridine and 4-*t*-butylpyridine (Reilly Tar and Chemical Co.) were used without further purification.

***trans-Co}(\text{acac})\_2\text{NO}\_2(\text{amine})*.**—Five grams of  $\text{Na}[\text{trans-Co}(\text{acac})_2(\text{NO}_2)_2]$  (0.013 mol) was dissolved in 100 ml of distilled water, and 3.2 g of pyridine (0.040 mol) or 5.4 g of 4-*t*-butylpyridine (0.040 mol) was added to the solution. In order to prevent formation of an oily product, 25 ml of methanol was added to the latter solution. The resulting mixture was stirred at 25° for 1 hr and then filtered. The red-brown solid was washed with two 50-ml portions of distilled water, a little acetone, and then ether and air dried. The yield was 4.3 and 4.9 g, respectively, 85% based on the original cobalt complex.

**Anal.**<sup>7</sup> Calcd for  $\text{C}_{15}\text{H}_{19}\text{O}_6\text{N}_2\text{Co}$  [ $\text{Co}(\text{acac})_2\text{NO}_2\text{py}$ ]: C, 47.13; H, 5.01; N, 7.33. Found: C, 46.89; H, 4.97; N, 7.33 (mp 169°). Calcd for  $\text{C}_{19}\text{H}_{26}\text{O}_6\text{N}_2\text{Co}$  [ $\text{Co}(\text{acac})_2\text{NO}_2\text{bpy}$ ]: C, 52.18;

(1) Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

(2) Abbreviations used in this paper include: acac, 2,4-pentanedionato (acetylacetonato); py, pyridine; bpy, 4-*t*-butylpyridine.

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(6) L. J. Boucher and E. P. McGovern, unpublished results.

(7) Elemental Analyses by Galbraith Laboratories, Inc., Knoxville Tenn.