According to Gschneidner and Valletta[8] 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 $GdSb_2$, $TbSb_2$, and $DySb_2$, 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.[8,9] There are, of course, no 4f electrons in yttrium.

Acknowledgment.—Thanks are extended to the Army Research Office (Durham) for financial support of this research.

[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.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
BRIGHAM YOUNG UNIVERSITY, PROVO, UTAH 84601

High-Pressure Th_3P_4-Type Polymorphs of Rare Earth Sesquiselenides

BY NORMAN L. EATOUGH[1] AND H. TRACY HALL

Received September 3, 1969

Previous work has shown that the normal monoclinic and rhombohedral forms of rare earth sesquisulfides could be converted to the more dense Th_3P_4-type cubic structure by high-pressure–high-temperature techniques.[2] Also, the Th_3P_4 forms of Ho_2Se_3 and Er_2Se_3 have been synthesized from the elements using high-pressure techniques.[2] We have now succeeded in preparing Tm_2Se_3, Yb_2Se_3, Lu_2Se_3, and Y_2Se_3 in the Th_3P_4-type structure by applying high pressure–high temperature to a stoichiometric mixture of the elements. Consequently, all the rare earth sesquiselenides except Eu_2Se_3 are now known in the Th_3P_4 structure.

Experimental Section

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

Results and Discussion

TABLE I

CUBIC RARE EARTH SESQUISELENIDES

	Pressure, kbars	Temp, °C	Lattice parameter, Å
Y_2Se_3	70	1800	8.6626 ± 0.0008
Tm_2Se_3	70	1800	8.5992 ± 0.0007
Yb_2Se_3	80	1800	8.615 ± 0.002
Lu_2Se_3	90	1800	8.570 ± 0.003

The Th_3P_4-type polymorphs of Y_2Se_3, Tm_2Se_3, Yb_2Se_3, and Lu_2Se_3 have been synthesized from stoichiometric mixtures of the elements using the conditions 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.*,[5] found the sesquiselenide series from Gd_2Se_3 to Dy_2Se_3 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.[2,6] It can be seen that Y_2Se_3 fits well at an ionic radius of 0.915 Å which is the same value as previously obtained for the sesquisulfide.[2] Ionic radii for the other rare earths were taken from Templeton and

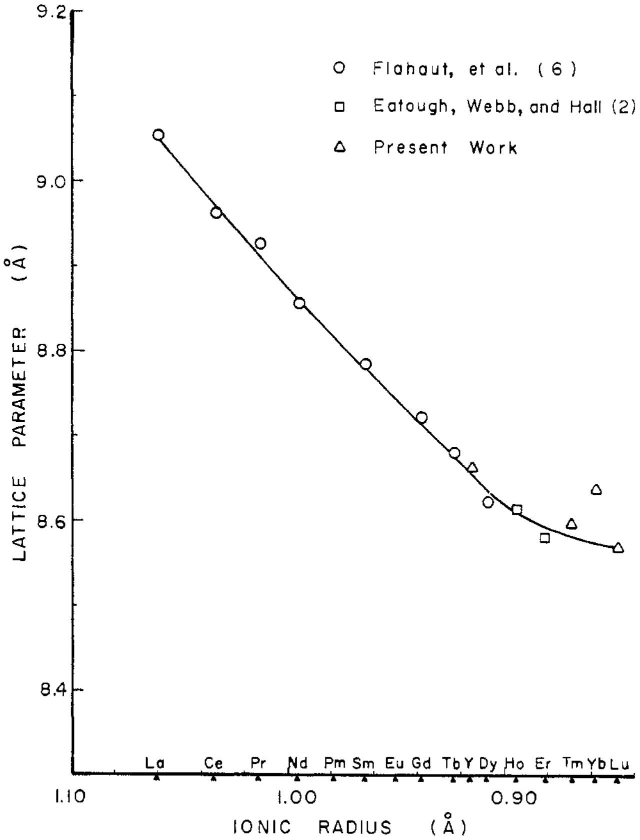

Figure 1.—Variation of lattice parameter with ionic radius of the Th_3P_4-type rare earth sesquiselenides.

---

[1] California State Polytechnic College, San Luis Obispo, Calif.

[2] N. L. Eatough, A. W. Webb, and H. T. Hall, *Inorg. Chem.*, **8**, 2069 (1969).

[3] H. T. Hall, *Rev. Sci. Instr.*, **29**, 267 (1958).

[4] H. T. Hall, *ibid.*, **33**, 1278 (1962).

[5] M. Guittard, A. Benacerraf, and J. Flahaut, *Ann. Chim.*, **9**, 25 (1964).

[6] J. Flahaut, P. Laruelle, M. P. Pardo, and M. Guittard, *Bull Soc. Chim. France*, 1399 (1965).

Dauben.[7] The lattice parameters of Tm_2Se_3 and Lu_2Se_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 Yb_2Se_3 is somewhat greater than its neighbors which indicates some Yb^{2+} character in Yb_2Se_3. This same effect was also observed in Yb_2S_3.[2] A graph of the minumum pressure for synthesis of the cubic polymorphs as a function of ionic radius of the rare earth is shown in Figure 2. Values for Ho_2Se_3 and Er_2Se_3 were taken from Eatough, Webb, and Hall.[2] The synthesis of Ho_2Se_3, Er_2Se_3, and Tm_2Se_3 takes place at about the same pressure. According to Gschneidner and Valletta[8] 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.

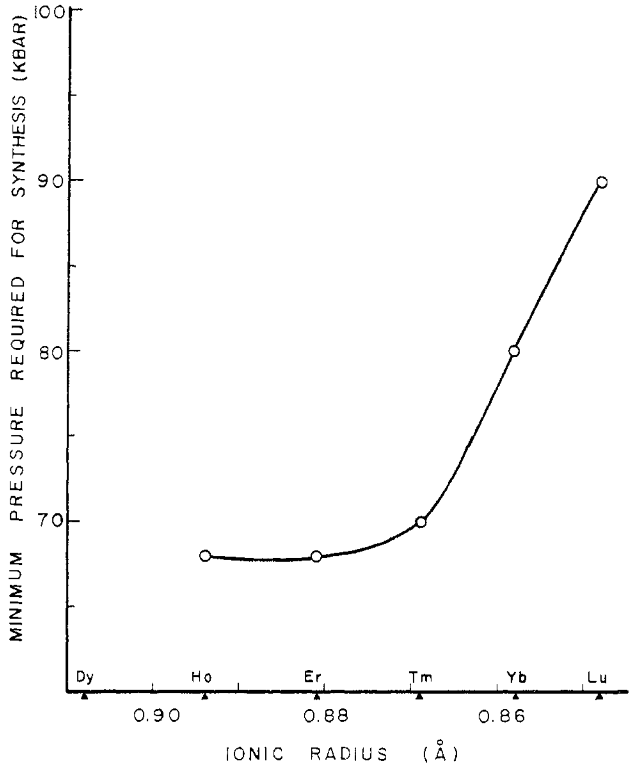

Figure 2.—Minimum pressure required for synthesis of cubic rare earth sesquiselenides.

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

---

(7) D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **76**, 5237 (1954).

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

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CARNEGIE-MELLON UNIVERSITY,
PITTSBURGH, PENNSYLVANIA 15213

Stereochemistry of β-Diketone Complexes of Cobalt(III). III. *cis* and *trans* Isomers of Nitroaminebis(acetylacetonato)cobalt(III)[1]

BY L. J. BOUCHER AND NYOLE G. PAEZ

Received September 15, 1969

The reaction of the anion[2] *trans*-$Co(acac)_2(NO_2)_2^-$ with a variety of amines leads rapidly to the exclusive formation of a *trans* product *via* the scheme[3-5]

$$\textit{trans}\text{-Co(acac)}_2(\text{NO}_2)_2^- + \text{H}_2\text{O} \rightleftarrows \textit{trans}\text{-Co(acac)}_2\text{NO}_2\text{H}_2\text{O} + \text{NO}_2^-$$

$$\textit{trans}\text{-Co(acac)}_2\text{NO}_2\text{H}_2\text{O} + \text{amine} \longrightarrow \textit{trans}\text{-Co(acac)}_2\text{NO}_2(\text{amine}) + \text{H}_2\text{O}$$

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

$$\textit{trans}\text{-Co(acac)}_2\text{NO}_2(\text{amine}) + \text{amine}' \rightleftarrows \textit{trans}\text{-Co(acac)}_2\text{NO}_2(\text{amine}') + \text{amine}$$

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.—Na[*trans*-$Co(acac)_2(NO_2)_2$] was prepared as previously described.[1] Reagent grade pyridine and 4-*t*-butylpyridine (Reilly Tar and Chemical Co.) were used without further purification.

***trans*-Co(acac)$_2$NO$_2$(amine).**—Five grams of Na[*trans*-$Co(acac)_2(NO_2)_2$] (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.[7] Calcd for $C_{15}H_{19}O_6N_2Co$ [$Co(acac)_2NO_2py$]: C, 47.13; H, 5.01; N, 7.33. Found: C, 46.89; H, 4.97; N, 7.33 (mp 169°). Calcd for $C_{19}H_{26}O_6N_2Co$ [$Co(acac)_2NO_2bpy$]: 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.

(3) L. J. Boucher and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **27**, 1093 (1965).

(4) L. J. Boucher, *Inorg. Chem.*, **6**, 2162 (1967).

(5) R. D. Archer and B. P. Cotsoradis, *ibid.*, **4**, 1584 (1965).

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

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