

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 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 Ho_2Se_3 and Er_2Se_3 were

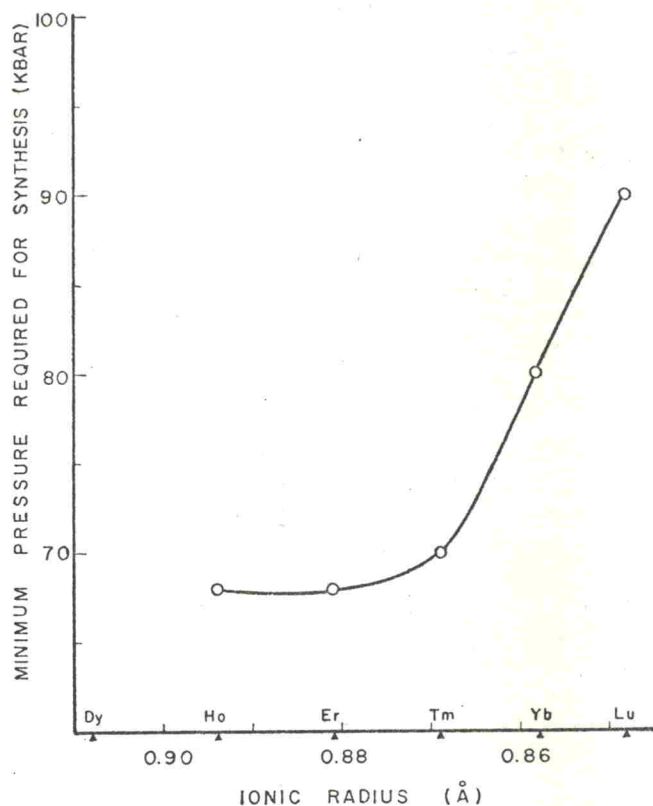


Figure 2.—Minimum pressure required for synthesis of cubic rare earth sesquiselenides.

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 Valletta⁸ 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.

(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).

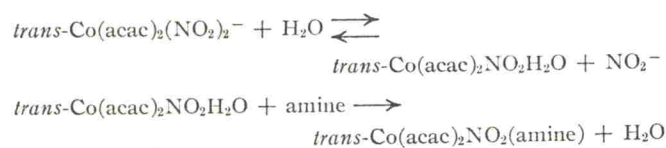
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CARNEGIE-MELLON UNIVERSITY,
PITTSBURGH, PENNSYLVANIA 15213

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

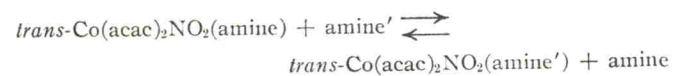
BY L. J. BOUCHER AND NYOLE G. PAEZ

Received September 15, 1969

The reaction of the anion² $\text{trans-Co}(\text{acac})_2(\text{NO}_2)_2^-$ with a variety of amines leads rapidly to the exclusive formation of a *trans* product via the scheme³⁻⁵



The above reactions appear to be an example of the octahedral *trans* effect of the nitro ligand. Although a previous study³ did not report an amine-exchange reaction, more careful work reveals that this reaction does occur rapidly at elevated temperatures as⁶



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.¹ 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.⁷ 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.

(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.