

yield of the octamethylene compound. The hydrobromides of the two last mentioned compounds were prepared from the crude reaction products and recrystallized from aqueous acetone.

The bis-pyridinium compounds listed in Table II were prepared by heating a mixture of the polymethylenebipyridine with the appropriate alkyl or aralkyl bromide in acetone or benzene. They were recrystallized from methanol-acetone.

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### The Preparation of Nickel(II) Thiocyanate Complex Compounds with Picolines and the Determination of their Heats of Formation<sup>1</sup>

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Work reported in an earlier paper<sup>3</sup> discussed the effect of negative groups upon the heat of formation of nickel(II) and cobalt(II) pyridinated compounds. We have now prepared a series of complexes in which the same metal salt has been combined with methyl substituted pyridines in an effort to determine the effect of the character of the base upon the heat of formation of the complexes. The heats of reaction of the simple salt, the amine and the complex with 2 *N* HCl were determined and the heat of formation of the complex calculated according to the equation

$$\Delta H_f = L_s + L_a - L_c$$

#### Preparation of Compounds

**Nickel(II) Di-2-methylpyridine Thiocyanate.**—17.48 g. (0.1 mole) of nickel thiocyanate was added to 300 ml. of  $\alpha$ -picoline (b.p. 128.4–130°). The mixture was maintained at 125 to 130° for four hours under a reflux condenser. The salt changed to a red color immediately on contact with the hot  $\alpha$ -picoline. The salt was completely dissolved after four hours heating producing a green solution. The solution was transferred to a large evaporating dish and low heating continued until a viscous mass was obtained. Rapid cooling produced a solid. The solid was pulverized and excess base removed in an air stream while the solid was continually stirred. The product, a brick red solid, was passed through a 60-mesh screen, air-dried for one-half hour. The compound may be kept indefinitely in a sealed container but will decompose almost quantitatively if left in the air overnight. The nickel content of this compound and others described later was determined by silver cyanide titration. *Anal.* Calcd. for Ni(SCN)<sub>2</sub>·2C<sub>6</sub>H<sub>7</sub>N: Ni, 16.25. Found: Ni, 16.07.

**Nickel(II) Tetra-3-methylpyridine Thiocyanate.**—The  $\beta$ -picoline available was the practical grade. Purification was effected by the method of Riethof.<sup>4</sup> The fraction distilling at 143–144° was collected for use in preparation of the complex compounds: 18.3 g. (0.077 mole) of NiCl<sub>2</sub>·6H<sub>2</sub>O was dissolved in 2 l. of H<sub>2</sub>O, 33 ml. of  $\beta$ -picoline was added, a deep blue solution was formed. A solution of 15 g. (0.1544 mole) of KSCN in 200 ml. of H<sub>2</sub>O was added slowly with constant stirring. A light blue microcrystalline pre-

cipitate formed immediately. The precipitate was obtained as a hard cake by use of a suction filter. The cake was pulverized and dried in air for four hours, then passed through a 60-mesh screen and placed in a desiccator over solid KOH for 2 days. The yield was nearly quantitative. The compound is stable in air for several days; at elevated temperatures it is readily converted to Ni(SCN)<sub>2</sub> and  $\beta$ -picoline. *Anal.* Calcd. for Ni(SCN)<sub>2</sub>·4C<sub>6</sub>H<sub>7</sub>N: Ni, 10.73. Found: Ni, 10.73.

**Nickel(II) Tetra-4-methylpyridine Thiocyanate.**—This compound was prepared in a manner identical to that described for the  $\beta$ -picoline complex. The color and characteristics of the compound are the same. *Anal.* Calcd. for Ni(SCN)<sub>2</sub>·4C<sub>6</sub>H<sub>7</sub>N: Ni, 10.73. Found: Ni, 10.77.

Attempts were made to prepare the above compounds by chloroform extraction as had been previously employed in the preparation of a number of pyridinated compounds. The compounds obtained by this method indicated some entrapment of chloroform in the crystals of the complex. The slow evaporation of a chloroform solution, obtained by the extraction of an aqueous suspension of the  $\beta$ -picoline compound, produced large blue transparent crystals. These crystals contained 8.7% nickel. Each preparation by this method produced the same product. Test for water in the crystals was negative. To check for the presence of chloroform, a pure sample of Ni(SCN)<sub>2</sub>·4BC<sub>6</sub>H<sub>7</sub>N prepared by precipitation from water, was dissolved in chloroform and the solution was evaporated. The large blue crystals obtained were crushed, then dried in air for an hour. Analysis showed 7.60% nickel. No attempt was made at the time to investigate the subject further since we were interested in the compound containing 4 molecules of the amine.

**Determination of Heats of Reaction.**—The method and the calorimeter employed in determining the heats of reaction of the Ni(SCN)<sub>2</sub>, the bases and the complexes with 2 *N* HCl were similar to those employed by Logan, Bush and Rogers in this Laboratory.<sup>3</sup> The values obtained and the heats of formation calculated from them are recorded in Table I.

### Results and Discussion

TABLE I

Substance	Heat of solution cal./mole at 25° <sup>a</sup>	Heat of formation cal./mole at 25°
$\beta$ -Picoline	−9200 (±50)	
$\gamma$ -Picoline	−9450 (±90)	
Pyridine <sup>b</sup>	−7860 (±25)	
Ni(CNS) <sub>2</sub>	1140 (±10)	
Ni(CNS) <sub>2</sub> ·4 $\beta$ -Pic	2340 (±60)	−36,000
Ni(CNS) <sub>2</sub> ·4 $\gamma$ -Pic	1450 (±40)	−38,110
Ni(CNS) <sub>2</sub> ·4Py <sup>b</sup>	7860 (±100)	−38,300

<sup>a</sup> Averages obtained from 3 to 5 determinations on each compound. <sup>b</sup> Reported in an earlier article (ref. 3).

The heats of formation of cobalt(II) (37,700 cal./mole) and nickel(II) (38,300 cal./mole) tetrapyridine thiocyanates and the cobalt(II) (22,300 cal./mole) and nickel(II) (18,500 cal./mole) hexapiperidine cyanates reported earlier, indicate that the negative groups play a more important role in the heat of formation of the complex compounds than do the metals. The fact that a stable tetra- $\alpha$ -picoline could not be obtained limited this study of the effect of bases on the heat of formation to the  $\beta$ - and  $\gamma$ -picolines. It is assumed that the proximity of the methyl group to the nitrogen atom in the amine prevented the formation of the tetra- $\alpha$ -picoline compound.

The relative basic strengths of pyridine,  $\beta$ -picoline and  $\gamma$ -picoline are evidenced by their heats of reaction with 2 *N* HCl recorded in Table I. By comparing the values calculated for the heats of formation of the complexes produced by the reaction of nickel thiocyanate with the three bases, Table I, it may be concluded that the heat of form-

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(2) This article is based on a thesis submitted by Don W. Carle in partial fulfillment of the requirements for the degree of Master of Science at Oregon State College, June, 1952.

(3) A. V. Logan, O. C. Bush and C. S. Rogers, *THIS JOURNAL*, **74**, 4194 (1952).

(4) G. Riethof, S. G. Richards, S. A. Savitt and D. F. Othmer, *Ind. Eng. Chem., Anal. Ed.*, **18**, 458 (1946).

ation of the nickel thiocyanate complex is practically independent of the amine used in its formation.

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### Tetramethyldisiloxane-1,3-diol

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A number of diorganosilane diols and tetraorganodisiloxane-1,3-diols have been prepared where one or more of the organic groups are larger than methyl.<sup>1-4</sup> However silane diols containing only methyl groups are very susceptible to condensation and have not been reported. We have now found that tetramethyldisiloxane-1,3-diol (I), the dimer of dimethylsilanediol, can be obtained in 60% yield by adding dimethyldichlorosilane to excess cold water maintained near neutrality by simultaneously adding ammonia. The compound is a snow-white crystalline solid, m.p. 67-68°, which may be stored, when pure, at room temperature without decomposition. The compound dissolves in water, but crystallizes from a cold aqueous solution upon the addition of salt.

The structure of the compound was shown by elemental analysis and determination of molecular weight and active hydrogens. On heating alone or in an inert solvent a mole of water is eliminated per mole of disiloxanediol with the formation of dimethylpolysiloxanes. Refluxing the compound with *n*-butanol and an acidic catalyst resulted in rapid dehydration and slow alcoholysis to form dimethyldibutoxysilane.

#### Experimental

**Preparation of Tetramethyldisiloxane-1,3-diol.**—Fifteen liters of water was placed in a flask equipped with a high speed stirrer and surrounded by an alcohol-Dry Ice cooling bath. Brom thymol blue and phenolphthalein indicators were added and the water was cooled to 2°. Ten moles of dimethyldichlorosilane was slowly added from a dropping funnel with rapid stirring. The dimethyldichlorosilane hydrolyzed almost instantly and the hydrogen chloride generated was neutralized with gaseous ammonia bled in from a cylinder through a glass tube which dips well below the surface of the water. The addition of the chlorosilane and ammonia was adjusted so that color of solution was in the blue range, pH 6.5-8.5. The addition of the silane required 48 minutes during which time the reaction temperature was kept at 0 to 2° and bath temperature at -30 to -40°. Five thousand grams of salt was added, and the reaction mixture was allowed to stand 24 hours at 10°. The crystalline mass which separated was filtered and taken up in two liters of boiling hexane. Upon cooling the hexane solution to 10° 494 g. of tetramethyldisiloxane-1,3-diol separated as snow-white needles. A sample for analysis was recrystallized from hexane, m.p. 67-68°.

*Anal.* Calcd. for C<sub>4</sub>H<sub>14</sub>O<sub>3</sub>Si<sub>2</sub>: C, 28.91; H, 8.49; Si, 33.78; mol. wt., 166.27; hydroxyl, 20.4. Found: C, 28.9, 29.2; H, 8.3, 8.5; Si, 33.61 (average of 12 determinations); mol. wt., 176 (in phenol), 171 (in camphor), 170 (in dioxane); hydroxyl (Zerewitinoff), 20.2.

**Condensation of (I).**—Refluxing of 16.6 g., 0.10 mole, of (I) in 100 ml. of dry benzene containing 1 g. of *p*-toluene-

sulfonic acid in a flask equipped with a Birdwell-Sterling water trap resulted in the formation in 20 minutes of a maximum 1.8 ml. of water. This is the theoretical amount required for complete dehydration to form dimethylpolysiloxanes.

**Alcoholysis of (I).**—Fifty-hour refluxing of 16.6 g., 0.10 mole, of (I) in a dry solution of 0.5 g. of *p*-toluenesulfonic acid in 100 ml. of *n*-butanol and 25 ml. of benzene resulted in the separation of 4.8 ml. of water of which 1.8 ml., 0.10 mole, separated in the first few minutes. No water was formed by refluxing the reactants in the absence of (I). Independent experiments showed that the rapid elimination of 0.1 mole of water was largely due to self-condensation of (I) and that the slow elimination of water that followed was due to the alcoholysis of the condensation products. Complete alcoholysis of 0.1 mole of (I) to dimethyldibutoxysilane would yield 5.4 ml. of water as compared to 4.8 ml. obtained. A larger run, in which the reaction mixture was neutralized and distilled, resulted in the isolation of dimethyldibutoxysilane (b.p. 190-200°; Si found 13.7 and 13.4, theory 13.73) together with a probable mixture of the latter with 1,3-dibutoxytetramethyldisiloxane,<sup>5</sup> b.p. 200-216°; Si found 17.7 and 17.6, theory 20.15.

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(5) R. O. Sauer, *THIS JOURNAL*, **68**, 138 (1946).

NEW PRODUCT DEVELOPMENT LABORATORY  
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### X-Ray Studies of Rare Earth Oxide Systems. II. The Oxide Systems Ce<sup>IV</sup>-Sm<sup>III</sup>, Ce<sup>IV</sup>-Gd<sup>III</sup>, Ce<sup>IV</sup>-Y<sup>III</sup>, Pr<sup>IV</sup>-Y<sup>III</sup> and Pr<sup>III</sup>-Y<sup>III</sup>

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Solid solutions of the trivalent rare earth oxides La<sub>2</sub>O<sub>3</sub>, Ce<sub>2</sub>O<sub>3</sub>, Pr<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub> and Sm<sub>2</sub>O<sub>3</sub> in the tetravalent rare earth oxides CeO<sub>2</sub> and PrO<sub>2</sub> have been studied by a number of investigators.<sup>1-10</sup> Although the separate studies have involved the use of X-ray powder photographs, density determinations and measurement of electric conductivities, complete studies of all of these systems have not as yet been reported. All of the systems studied show a homogeneous region with the fluorite structure from the pure tetravalent oxide to about 60 atom per cent. of the trivalent oxide. The deficiency of oxygen caused by substitution of M<sup>III</sup> for M<sup>IV</sup> in the fluorite structure leads to random vacancies in the anion lattice. This contention is supported by the relative intensities of the X-ray diffraction lines<sup>1,9</sup> and by the correlation of density measurements with the lattice constants.<sup>1,7</sup>

The present communication reports an extension of the X-ray studies to some trivalent rare earth ions of smaller radius. Yttrium has been included because of its great similarity to the rare earth elements of higher atomic number and because of its

(1) E. Zintl and U. Croatto, *Z. anorg. Chem.*, **242**, 79 (1939).

(2) U. Croatto, *Ricerca Sci.*, **12**, 830 (1942).

(3) U. Croatto and A. Mayer, *Gazz. chim. ital.*, **73**, 199 (1943).

(4) U. Croatto, *ibid.*, **73**, 257 (1943).

(5) U. Croatto, *ibid.*, **74**, 20 (1944).

(6) U. Croatto and M. Bruno, *ibid.*, **76**, 246 (1946).

(7) U. Croatto and M. Bruno, *Proc. Intern. Congr. Pure and Applied Chem. (London)*, **11**, 69 (1947).

(8) U. Croatto and M. Bruno, *Gazz. chim. ital.*, **78**, 83 and 95 (1948).

(9) J. D. McCullough, *THIS JOURNAL*, **72**, 1386 (1950).

(10) Maria Bruno, *Ricerca Sci.*, **20**, 645 (1950).

(1) R. Robinson and F. S. Kipping, *Proc. Chem. Soc.*, **28**, 245 (1912).

(2) R. Robinson and F. S. Kipping, *J. Chem. Soc.*, **101**, 2156 (1912).

(3) P. A. Digorgio, Abstract of paper presented Am. Chem. Soc. meeting, April, 1946, Atlantic City.

(4) N. W. Cusa and F. S. Kipping, *J. Chem. Soc.*, 2205 (1932).