

1-(2,4-Dinitrophenyl)-3-(*p*-dimethylaminophenyl)-5-pyrazolone was prepared by treating 0.5 g. of IV with 1 g. of 2,4-dinitrophenylhydrazine and 2 ml. of concentrated hydrochloric acid in 15 ml. of ethanol. An orange-red precipitate immediately formed changing quickly to a dark purple-red. It was recrystallized from methanol yielding 0.4 g. (52%), m.p. 243–244°.

*Anal.* Calcd. for  $C_{17}H_{15}O_5N_5$ : N, 18.96. Found: N, 18.62.

3-(*p*-Dimethylaminophenyl)-5-isoxazolone was prepared by refluxing 0.7 g. of IV and 0.5 g. of hydroxylamine hydrochloride in 10 ml. of ethanol for one hour. On cooling and scratching the inner wall of the flask with a glass rod, 0.3 g. (50%) of white needles was obtained, m.p. 164°.

*Anal.* Calcd. for  $C_{11}H_{12}O_2N_2$ : N, 13.72. Found: N, 13.52.

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### *trans*-Dichlorobis-(N- or C-alkylethylenediamine)-cobalt(III) Chlorides<sup>1</sup>

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During the course of some investigations on the mechanism of substitution reactions in complex ions<sup>2,3</sup> it became of interest to compare the rates of reaction for an analogous series of compounds. Since *trans*-dichlorobis-(ethylenediamine)-cobalt(III) chloride<sup>4</sup> is one of the more readily available complexes suitable for this purpose, it was decided to attempt the synthesis of similar substituted ethylenediamine compounds. The preparation of some C-substituted ethylenediamine complexes<sup>5,6</sup> of this type have been described but no report was found for the synthesis of N-alkylethylenediamine derivatives. However, Keller and Edwards<sup>7</sup> have recently described the preparation of tris-(N-alkylethylenediamine)cobalt(III) salts.

An account is given in this paper of the method of synthesis and some properties of *trans*-dichlorobis-(substituted-ethylenediamine)-cobalt(III) chlorides. The diamines employed and the symbolization used here are indicated below.

Diamine	Symbol
$CH_3NHCH_2CH_2NH_2$	N-Meen
$CH_3CH_2NHCH_2CH_2NH_2$	N-Eten
$CH_3CH_2CH_2NHCH_2CH_2NH_2$	N- <i>n</i> -Pren
$NH_2C(CH_3)_2CH_2NH_2$	Iso-bn
$NH_2C(CH_3)_2C(CH_3)_2NH_2$	Tetra-Meen

Attempts to prepare corresponding compounds with N-isopropylethylenediamine and N-*n*-butylethylenediamine were not successful. Addition of N-isopropylethylenediamine to an aqueous solution of cobalt(II) chloride resulted in the separation of a gelatinous precipitate of cobalt(II) hydroxide. Although the reaction with N-*n*-butylethylene-

(1) This investigation was supported by a grant from the United States Atomic Energy Commission under Contract AT(11-1)-89-Project No. 2.

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(7) R. N. Keller and L. J. Edwards, *THIS JOURNAL*, **74**, 215 (1952).

diamine appears to proceed as with the lower alkylethylenediamines, it was not possible to isolate a crystalline product from the final green concentrate.

These green substituted ethylenediamine salts resemble the corresponding *trans*-dichlorobis-(ethylenediamine)-cobalt(III) chloride in color as shown by their similar absorption spectra (Fig. 1). The salts are all soluble in methanol and extremely soluble in water. Aqueous solutions of the N-alkylethylenediamine complexes turn red or aquate at about the same rate as does *trans*-[Coen<sub>2</sub>Cl<sub>2</sub>]Cl while the isobutylethylenediamine and tetramethylethylenediamine derivatives aquate much more rapidly.<sup>8</sup>

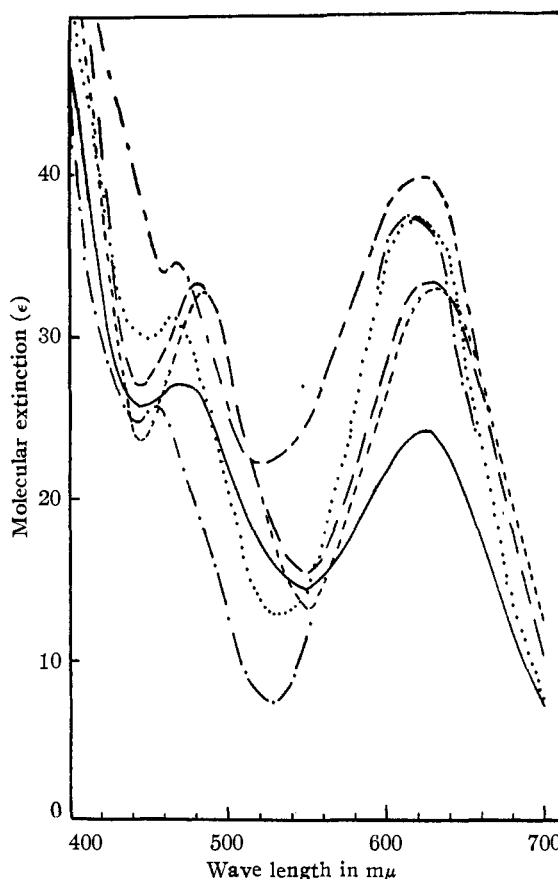


Fig. 1.—Absorption spectra of *trans*-[Co(AA)<sub>2</sub>Cl<sub>2</sub>]Cl complexes in methanol solution: en (0.0071M) --; N-Meen (0.0068M), —; N-Eten (0.0053M), — —; N-*n*-Pren (0.0050M), - - - -; iso-bn (0.0057M), .....; tetra-Meen (0.0058M), — — —.

These green salts crystallize from acid solution as hydrogen chloride addition compounds but lose this adduct less readily than does the corresponding *trans*-[Coen<sub>2</sub>Cl<sub>2</sub>]Cl·HCl. In fact even after heating the solid at 110° overnight, the complexes still contain as much as a half a mole of hydrogen chloride. No attempt was made to liberate all of the hydrogen chloride by either prolonged heating or use of a higher temperature. Finally, in no case was the *trans* isomer converted to the *cis* complex. The usual procedure<sup>4</sup> of

(8) Quantitative studies on these rates of aquation will soon be reported in *THIS JOURNAL*.

evaporating an aqueous solution of the *trans* complex was followed but in every instance a green glass-like residue was obtained. It may be argued that the *cis* isomer is not obtained due to the use of *trans* salts which have not been completely freed of hydrogen chloride. However, even when the residue was redissolved and the evaporation procedure repeated several times in an attempt to liberate the slight excess of hydrogen chloride, there still was no sign of any purple *cis* compound.

#### Experimental

**Substituted Ethylenediamines.**—The anhydrous N-alkylethylenediamines were obtained from Mr. R. Kent Murmann.<sup>9</sup> The dihydrochlorides of isobutylenediamine and tetramethylethylenediamine were furnished by Dr. Yun-Ti Chen and R. Kent Murmann, respectively. These hydrochlorides were converted to the free amine by the treatment of concentrated aqueous solutions of the salt with an excess of solid sodium hydroxide. The mixture was in turn extracted with ether and finally the ether removed with the aid of a water aspirator. The residual-free amine was used without further purification.

***trans*-Dichlorobis-(N-alkylethylenediamine)-cobalt(III) Chlorides.**—The procedure described here for the preparation of *trans*-dichlorobis-(N-methylethylenediamine)-cobalt(III) chloride was likewise employed in the synthesis of corresponding ethyl and *n*-propyl derivatives. A solution of 7.5 g. of N-methylethylenediamine in 70 cc. of water was added to 50 cc. of a solution containing 16 g. of cobalt(II) chloride hexahydrate. A stream of air previously washed with water was slowly bubbled through the dark brown opaque reaction mixture for eight hours. At the end of this time 35 cc. of concentrated hydrochloric acid was added to the mixture and the acid solution was concentrated on a steam-bath. The green viscous concentrate was dissolved in 20 cc. of methanol and absolute ethanol was added just short of causing the separation of a green oil (approximately 75 cc.). The solution was allowed to stand overnight during which time a green crystalline product separated. This salt was collected on a filter washed with absolute ethanol followed by ether and dried overnight at 110°. A yield of 7 g. or 40% based on the diamine was obtained. *Anal.* Calcd. for [Co(N-Meen)<sub>2</sub>Cl<sub>2</sub>]Cl·0.1HCl: Cl, 37.1. Found: Cl, 37.3.

In the same manner a yield of 28% of *trans*-dichlorobis-(N-ethylethylenediamine)-cobalt(III) chloride was isolated. *Anal.* Calcd. for [Co(N-Eten)<sub>2</sub>Cl<sub>2</sub>]Cl·0.6HCl: Cl, 35.2. Found: Cl, 35.4.

The yield of *trans*-dichlorobis-(N-*n*-propylethylenediamine)-cobalt(III) chloride was 36%.

*Anal.* Calcd. for [Co(N-*n*-Pren)<sub>2</sub>Cl<sub>2</sub>]Cl·0.5HCl: Cl, 32.2. Found: Cl, 32.2.

***trans*-Dichlorobis-(isobutylenediamine)-cobalt(III) Chloride.**—A solution of 5 g. of isobutylenediamine in 15 cc. of water was added to that of 5 g. of cobalt(II) chloride in 20 cc. This mixture was then treated with 5 cc. of 30% hydrogen peroxide. A vigorous exothermic reaction occurred accompanied by the voluminous evolution of oxygen. After standing for 1 hr. at 60° the reaction mixture was made acid by the addition of 15 cc. of concentrated hydrochloric acid. This solution was concentrated on a steam-bath until crystals began to separate at which time the concentrate was removed from the bath and allowed to stand at room temperature overnight. The crystalline product was finally collected on a filter, washed with absolute ethanol and ether, then dried overnight at 110°. The product weighed 2 g. or was obtained in only a 19% yield. *Anal.* Calcd. for [Co(iso-bn)<sub>2</sub>Cl<sub>2</sub>]Cl·0.5HCl: Cl, 33.7. Found: Cl, 33.9.

***trans*-Dichlorobis-(tetramethylethylenediamine)-cobalt(III) Chloride.**—A small amount of crystalline material separated upon the addition of 5 g. of tetramethylethylenediamine in 10 cc. of water to a 20-cc. solution containing 5 g. of cobalt(II) chloride. However, this substance is completely dissolved during the gradual addition of 5 cc. of 30% hydrogen peroxide to the mixture. Unlike the procedure followed above this reaction mixture did not yield the desired *trans* complex when treated directly with concentrated hydrochloric acid. Instead it was found necessary to first

allow the solution to concentrate to dryness at 60°. This residue was then extracted with 10 cc. of concentrated hydrochloric acid and the less soluble green salt collected on a filter. This crystalline material was dissolved in a minimum amount of methanol and then an excess of ether was added to the solution. After standing in an ice-salt-bath for several hours, the green product was collected, washed with ether and dried overnight, at 110°. The dry salt weighed 3.5 g. or was obtained in a 39% yield. *Anal.* Calcd. for [Co(tetra-Meen)<sub>2</sub>Cl<sub>2</sub>·0.6HCl]: Cl, 30.5. Found: Cl, 30.6.

**Spectral Measurements.**—All measurements were made with a Beckman model DU spectrophotometer in silica cells having a 1-cm. light path. Extinction coefficients were calculated from the familiar equation

$$\epsilon = 1/cd \log_{10} (I_0/I)$$

Methanol was used as a solvent and measurements were made at room temperature.

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### The Behavior of Tetraborane toward Trimethylamine and Ethanol

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In the search for more knowledge of the chemistry of tetraborane (B<sub>4</sub>H<sub>10</sub>)—especially with reference to structural implications—we have found that it reacts according to the equation B<sub>4</sub>H<sub>10</sub> + (3 + x) (CH<sub>3</sub>)<sub>3</sub>N → 3(CH<sub>3</sub>)<sub>3</sub>NBH<sub>3</sub> + BH<sub>3</sub>·x(CH<sub>3</sub>)<sub>3</sub>N when it is added to trimethylamine (excess) dissolved in tetrahydrofuran at -78°. A similar, but less stoichiometric, result was obtained when the solvent was omitted, or when a deficiency of trimethylamine was used. The value of x ranged from 0.54 to 0.37; this trimethylamine was retained *in vacuo* at room temperature, in the white or yellowish polymeric solid. Non-volatile B-H material was obtained also when tetraborane was allowed to react with an amount of ethanol too small for complete solvolysis, forming also hydrogen, diethoxyborane and triethyl borate.

From these results, it appears that tetraborane behaves like diborane, except that it furnishes three BH<sub>3</sub> groups for reaction, instead of two, and leaves polymeric material as a by-product. It is difficult to conceive of a B<sub>4</sub>H<sub>10</sub> structure in which three essentially intact BH<sub>3</sub> groups are attached to a BH unit by conventional bonds; hence the easy delivery of three BH<sub>3</sub> groups may well be due to a very labile structure which shifts easily to make them available for reaction. In fact, it is possible to write a structure based upon the principles recognized in B<sub>5</sub>H<sub>9</sub>,<sup>1,2</sup> such that three BH<sub>3</sub> groups would result solely from the breaking of B-H-B bridge bonds; and such a structure is consistent with preliminary results of the electron-diffraction study of tetraborane.<sup>3</sup>

In none of our experiments was it possible to find any evidence of compounds involving a covalent B-B bond of unit order. It appears that any unique B-B bond in tetraborane must be extremely

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