

pared by known procedures.³ All pyridine and pyridine N-oxide complexes were recrystallized from chloroform-pentane; they are characterized in Table I. *trans*-1,3-Dichloro-2-(*cis*-2-butene)-4-piperidineplatinum(II) was prepared by dissolving 0.5 mmole of $K(C_4H_9)PtCl_3$ in water at 0–5° and adding a solution of 0.05 ml of piperidine in 5 ml of water, slowly with stirring. The yellow precipitate was washed with water and dried. It is relatively soluble in pentane. *Anal.* Calcd for $C_9H_{19}PtCl_2$: C, 26.54; H 4.70. Found: C, 26.49; H, 4.64. The infrared spectrum determined in halocarbon mull showed the C=C stretching frequency at 1522 cm^{-1} .

Spectra.—All spectra were determined with a Perkin-Elmer grating spectrophotometer, Model 337, with expanded scale and polystyrene calibration. The pyridine complexes were examined in $DCCl_3$ in matched KBr cells; the complexes were also examined as halocarbon mulls. Because of solubility difficulties, pyridine N-oxide complexes were determined as halocarbon mull spectra with KBr plates; the complexes were also examined in KBr pellets. The mull spectra and the KBr pellets always gave essentially the same spectra. We consider the spectra to be accurate within $\pm 2\text{ cm}^{-1}$.

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Five-Coordinated High-Spin Complexes of Cobalt(II) Iodide and Thiocyanate with 2,2',2''-Triaminotriethylamine

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Some years ago Barclay and Barnard¹ isolated the compounds $Co(tren)I_2$ and $Co(tren)(NCS)_2$,² having magnetic moments 4.8 BM. Octahedral or tetrahedral structures were proposed because these were the only known stereochemical configurations compatible with a high-spin electronic configuration. In later thermodynamic studies of formation of 1:1 complexes in aqueous solution with tren and bivalent 3d metal ions, evidence was found to indicate the presence of five-coordinated species of the type $[M(H_2O)(tren)]^{2+}$, when $M = Co, Zn$.³ The five-coordinated structure of the cobalt-tren ion in aqueous solution has recently been confirmed by the similarity of its absorption spectrum³ with that of the solid compound $[Co(Me_6tren)Br]Br^{2,4}$ which has been shown by X-ray studies⁵ to possess a trigonal-bipyramidal structure. Thus the existence of the five-coordinated species $[Co(H_2O)(tren)]^{2+}$ in aqueous solution (a highly coordinating solvent which should favor six-coordination) prompted

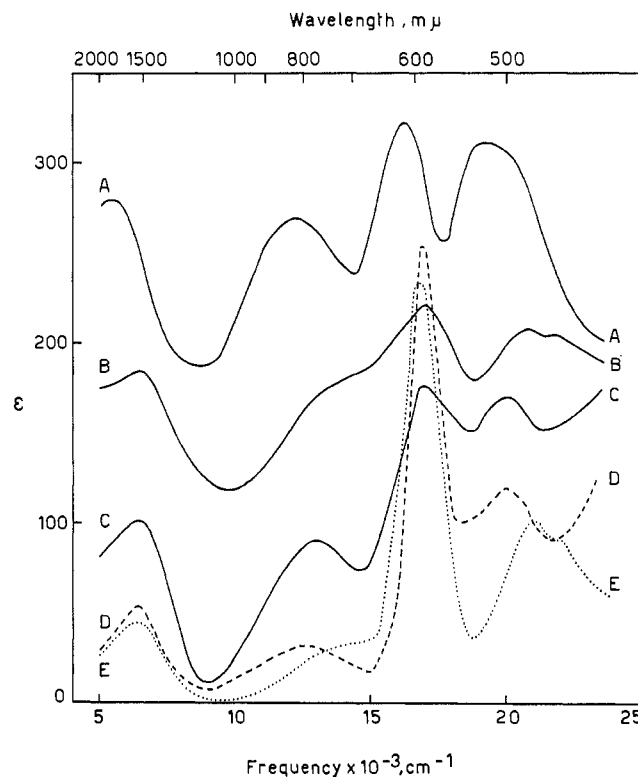


Figure 1.—Electronic spectra of some five-coordinated cobalt complexes: A, reflectance spectrum of $[Co(Me_6tren)Br]Br$; B, reflectance spectrum of $[Co(tren)(NCS)]SCN$; C, reflectance spectrum of $[Co(tren)I]I$; D, absorption spectrum of $[Co(tren)I]I$ in nitroethane; E, absorption spectrum of $[Co(tren)(NCS)]SCN$ in nitroethane. Arbitrary scale of absorbance for reflectance spectra.

us to investigate whether Barclay and Barnard's compounds were also five-coordinated.

The iodide and thiocyanate cobalt-tren complexes behave as 1:1 electrolytes in nitroethane, in which the molar conductivity for solutions about 10^{-3} M at 20° are 63 and 69 $\text{cm}^2\text{ ohm}^{-1}\text{ mole}^{-1}$, respectively. Under the same conditions the reference electrolyte $[(n-C_4H_9)_4N]Br$ exhibits a molar conductivity of 70 $\text{cm}^2\text{ ohm}^{-1}\text{ mole}^{-1}$. These compounds are thus to be formulated as $[Co(tren)X]X$, where $X = I, NCS$.

The ligand field spectra of these compounds in the solid state are equivalent with their solution spectra (Figure 1). The stereochemistry of these complexes must therefore be essentially the same in the solid state and in solution. The spectra of the complexes $[Co(tren)X]X$ are very different from those of the cobalt compounds with tetrahedral or octahedral stereochemistry.⁶ They are instead very similar to the spectrum of the five-coordinated complex $[Co(Me_6tren)Br]Br$ (Figure 1). It is to be noted that all of the bands of these tren complexes are shifted to higher frequencies with respect to the Me_6tren complex. This is in accord with the greater crystal field strength of the NH_2 group in comparison with the $N(CH_3)_2$ group.⁷ For the tren complexes, furthermore, the major frequency shifts between the peaks of the isothiocyanate and

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iodide spectra are found in the second ($\approx 13,000\text{ cm}^{-1}$) and fourth bands ($\approx 20,000\text{ cm}^{-1}$). Previous studies⁸ have shown that these two bands are the most sensitive to the strength and symmetry of the field produced by the ligands.

It is therefore proposed that the complexes $[\text{Co}(\text{tren})\text{I}]\text{I}$ and $[\text{Co}(\text{tren})(\text{NCS})]\text{SCN}$ are five-coordinated, with tren acting as a tetradentate ligand.

Infrared spectra give additional support to this formulation for the thiocyanate compound. This complex exhibits two bands at 2085 and 808 cm^{-1} , which are attributed to the CN and CS stretching frequencies of the N-bonded NCS ion.⁹ Another band found at 2060 cm^{-1} is assigned to the CN stretching frequency of the free SCN^- ion.⁹ The CS frequency of the free SCN^- ion usually occurs at about 745 cm^{-1} but is presumably masked by the absorption bands of the ligand in this region.¹⁰ The frequencies exhibited in the $[\text{Co}(\text{tren})(\text{NCS})]\text{SCN}$ infrared spectrum are almost the same as those found for $[\text{Cu}(\text{tren})(\text{NCS})]\text{SCN}$, whose structure has recently been found to be five-coordinated by X-ray crystal structure studies.¹¹ The copper complex exhibits bands at 2095 , 2060 , and 818 cm^{-1} .¹²

In conclusion, the tren complexes of cobalt(II), copper(II),^{4,11} and probably zinc(II)³ can exhibit the unusual coordination number five. In contrast, X-ray studies¹³ and spectral evidence¹⁴ indicate that all of the nickel-tren complexes which have been studied are octahedral. The structural studies of manganese(II) and iron(II) complexes with tren are sparse but, at least in aqueous solution, seem to indicate octahedral structures.³ This is in accord with the results of a calorimetric study¹⁵ of the relative stability of five- and six-coordination of bivalent metals from manganese to zinc. The results show that five-coordination is favored in the order $(\text{Co}, \text{Cu}, \text{Zn}) > (\text{Fe}, \text{Ni}) > \text{Mn}$. The stereochemical requirements of tren thus allow five-coordination for the three elements forming the most stable five-coordinated complexes. By increasing the bulkiness of the ligand through N-methylation, five-coordinated complexes for all of the transition metal ions from manganese(II) to zinc(II) are obtained.

Experimental Section

The complexes $[\text{Co}(\text{tren})\text{X}]\text{X}$, where $\text{X} = \text{I}$ or NCS , were prepared by the procedure of Barclay and Barnard¹ and analyzed satisfactorily for nitrogen. The absorption spectra were recorded with a Beckman DK2 spectrophotometer and 5-cm silica cells. The solutions of the complexes in nitroethane were about 10^{-3} M . The diffuse-reflectance spectra were measured using the standard Beckman reflectance attachment and magnesium oxide as the reference. The infrared spectra were recorded on

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Nujol mulls using a Perkin-Elmer 337 spectrophotometer. The conductivity values were measured on a WTW Model LBR/B conductivity bridge. All operations on the solutions were performed in an atmosphere of pure nitrogen.

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Bis(tetrahydrofuran)-Haloalanes

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Mono- and diamine adducts of alane, AlH_3 , and haloalanes are known and have been investigated;¹⁻⁴ however, little is known about their ether adducts. Alane does not form well-defined diethyl etherates⁵ and the bis(tetrahydrofuran) adduct⁶ is reported to be stable only below -5° . The present study concerns the preparation and characterization of some new, crystalline bis- and tris(tetrahydrofuran)-haloalanes.

Experimental Section

Reactants and products were handled in a dry nitrogen atmosphere. All solvents were distilled over lithium tetrahydroaluminum, LiAlH_4 , or sodium metal. The aluminum halides were purified by high-vacuum sublimation. The diethyl ether solvated hydride was prepared according to Schlesinger⁵ by using a 3:1 stoichiometric ratio of LiAlH_4 and aluminum chloride, AlCl_3 .

Elemental analyses were performed in our laboratories. Hydrolyses yielded active hydrogen and deuterium which were measured using a vacuum rack equipped with a Toepler pump and a calibrated system. Mass spectrometry confirmed the identity of the evolved gas. The nuclear magnetic resonance spectra were obtained from solutions on a Varian A-60 HR spectrometer. Infrared spectra were obtained on a Beckman IR 9 and IR 11. Fluorolube mulls were used for the $3800\text{--}1330\text{ cm}^{-1}$ region; Nujol mulls were used below 1330 cm^{-1} . X-Ray powder diffraction patterns were obtained using $\text{Cu K}\alpha$ radiation with a Debye-Scherrer camera having a 7.16-cm radius. The cryoscopic molecular weights in benzene were obtained using a modified standard apparatus⁷ containing a magnetic stirrer and loaded in a drybox. The freezing points were measured using a thermocouple and were reproducible to $\pm 0.01^\circ$. Ebulliometric molecular weights were obtained using a differential ebulliometer with thermopiles reproducible to $\pm 0.005^\circ$.

(1) Preparation of $\text{AlHX}_2 \cdot 2(\text{THF})$ and $\text{AlH}_2\text{X} \cdot 2(\text{THF})$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). Method A.—The preparation of $\text{AlHX}_2 \cdot 2(\text{THF})$ and $\text{AlH}_2\text{X} \cdot 2(\text{THF})$ requires the reaction of AlX_3 and AlH_3 in mole ratios of 2:1 and 1:2, respectively. For a typical example, $\text{AlHX}_2 \cdot 2(\text{THF})$ was prepared by adding 0.10 mole of solid alumi-

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