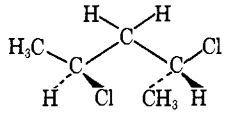
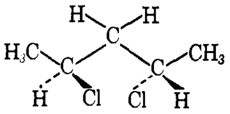
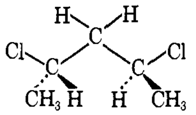
nance spectroscopy[10] in the case of the 2,4-dichloropentanes. Both methods show that the only eligible conformer for the *meso* isomer is structure I, *i.e.*, the *trans,gauche* structure and its analog, the *gauche,trans* form. The possible conformers for the *dl* form are structures II and III. However, the conformer represented by III appears to be absent since it could not be detected by infrared even at elevated temperatures.[3] This large energy difference was also confirmed by both nmr interpreted in terms of coupling constants and detailed calculations assuming interactions characterized by Lennard-Jones type potentials between nonbonded atoms and groups.[10] The conformer represented by II is favored over III by the factor $\eta^2 = 22.4$ using the equation[2] developed from statistical mechanical considerations. This high value of η certainly emphasizes the insignificance of III as a contributing conformer for the racemic diastereomer. As pointed out by Flory,[2] in the case of the diphenylpentanes the equilibration of the 2,4,6-trisubstituted heptane would be required for interpretation of the stereochemical equilibrium and distribution among conformers for higher homologs.



I



II



III

Finally, it is of interest to compare the stabilities of *erythro*- and *threo*-2,3-dichloropentanes. Usually, barring intramolecular interactions, the *erythro* diastereomer is expected to be slightly more stable.[5] Although the small amount of the 2,3 isomers (~10%) in equilibrium with the 2,4-dichloropentane diastereomers does not allow an accurate calculation of ΔG, the data roughly suggest that the diastereomers are of approximately equal stability.

Acknowledgment. The authors acknowledge the helpful discussion of this paper with Professor J. F. Bunnett. Thanks are also due to Mr. W. F. Tully for assistance with the gas chromatographic analyses.

[10] P. E. McMahon and W. C. Tincher, *J. Mol. Spectry.*, **15**, 180 (1965); P. E. McMahon, *ibid.*, **16**, 221 (1965).

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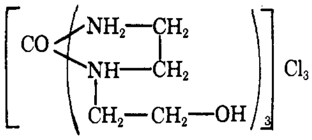
Complexes of N-Hydroxyethylethylenediamine

Sir:

Several workers have investigated the cobalt(III) complexes with N-hydroxyethylethylenediamine,[1] but agreement on the nature of these substances has not been reached. Keller and Edwards[2] reported the synthesis of $[Co(etolenH)_3]Cl_3$, by the aerial oxidation of a mixture of cobalt(II) chloride (1 mole), etolenH (5 moles), and hydrochloric acid (0.5 mole) in aqueous solution, using active charcoal as a catalyst. The product was obtained as orange crystals, insoluble in ethanol. Keller and Edwards formulated this compound as

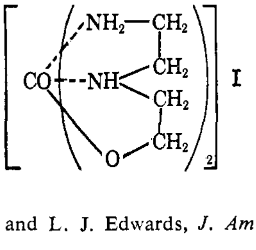


I

The uncoordinated hydroxy groups were reported to be unreactive toward several reagents which normally react with free hydroxyl groups. The Co(III) complex was reported to be stable in boiling concentrated acids, including aqua regia. Keller and Edwards also found that a solution of the compound turned purple on addition of caustic alkali.

Drinkard, Bauer, and Bailar[3] repeated this work during their investigation of the reactivity of organic hydroxy groups β to the coordination site in Co(III) complexes. The only product they could isolate from direct oxidation of a solution containing Co(II) and etolenH was proved to be tris(ethylenediamine)cobalt(III) chloride. Since their sample of purified etolenH was shown to contain no ethylenediamine, the latter must have resulted from a cleavage of a C–N bond of etolenH during the oxidation of Co(II). They showed that the reaction of 1 mole of hexaamminecobalt(III) chloride with 3 moles of etolenH in the presence of active charcoal gave a product which was extremely soluble in water and in ethanol. Analysis of their product, obtained as a red glass on dehydration over P_4O_{10}, agreed with the formula $[Co(etolenH)_3]Cl_3$ and was found to be inactive toward acetylation and benzoylation, like the product of Keller and Edwards. The red color is unusual for a complex containing six nitrogen atoms coordinated to Co(III), as in structure I, and was explained by an extensive effect of OH, strongly hydrogen bonded to a hydrogen atom in an NH_2 group. The hydrogen bonding supposedly also reduced the activity of the OH group.

Tennenhouse[4] reinvestigated the reaction of $[Co(NH_3)_6](NO_3)_3$ with etolenH. He found that the reaction of 2 moles of etolenH and 1 mole of complex in the presence of charcoal gave a purple solution which, upon the addition of sodium iodide in 50% ethanol solution, yielded a crystalline purple product. This gave an analysis corresponding to the formula $[Co(etolen)_2]$ I and was formulated as



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[1] 2-(2-Aminoethylamino)ethanol, $NH_2CH_2CH_2NHCH_2CH_2OH$, will be referred to as etolenH, where H is the hydroxy proton. Thus, etolen refers to $NH_2CH_2CH_2NHCH_2CH_2O^-$.

[2] R. N. Keller and L. J. Edwards, *J. Am. Chem. Soc.*, **74**, 215 (1952).

[3] W. C. Drinkard, H. F. Bauer, and J. C. Bailar, Jr., *ibid.*, **82**, 2992 (1960).

[4] G. J. Tennenhouse, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1963.

This formulation shows etolen as a tridentate ligand toward cobalt(III). The inactivity of coordinated etolen in the cobalt(III) complex is thus due to the fact that the complex does not contain a free hydroxy group.

The following etolenH and etolen⁻ complexes[5] were recently synthesized by us: $[Co(etolenH)_2(NO_2)_2]X$ (where $X = NO_2^-, NO_3^-, I^-$, or $(Co(etholenH)(NO_2)_4]^-)$, $[Co(etolenH)(etolen)]I_2$, $(Co(etolen)_2]I$, $(Ni(etolenH)_2]Br_2$, $[Pd(etolenH)Cl_2]$, $[Pd(etolenH)_2]Cl_2$, and $[Pt(etolen)_2]Cl_2$.

In view of the conflicting data on the cobalt(III) complex, the reactions of etolenH with Co(II) and Co(III) under several conditions of pH, temperature, concentration, catalyst, and solvents were studied critically. It is now apparent that at pH below 8, etolenH behaves as a bidentate ligand coordinated through the two nitrogen atoms. At pH above 8.5, a part or all of etolenH is coordinated as tridentate etolen⁻, coordinated through the oxygen atom as well as the two amino nitrogen atoms. In the case of Co(III), even etolenH may behave as a tridentate ligand. Depending on pH, the metal/ligand ratio, the catalyst, and the temperature of reaction, the following species are apparently capable of existence in the Co(III)–etolenH system.

$$\underset{\textbf{I}}{[Co(etolenH)_3]^{3+}} \xrightleftharpoons[+\text{etolenH}]{-\text{etolenH}} \underset{\textbf{II}}{[Co(etolenH)_2]^{3+}} \xrightleftharpoons[+\text{H}]{-\text{H}}$$

$$\underset{\textbf{III}}{[Co(etolenH)(etolen)]^{2+}} \xrightleftharpoons[+\text{H}]{-\text{H}} \underset{\textbf{IV}}{[Co(etolen)_2]^{+}}$$

We have not been able to isolate any pure Co(III) compound containing more than 2 moles of etolenH per cobalt atom. All of our attempts to synthesize tris(N-hydroxyethylethylenediamine)cobalt(III) chloride were unsuccessful. Direct oxidation of a solution containing cobalt(II) chloride and etolenH yielded $[Co(en)_3]^{3+}$, $[Co(etolenH)(etolen)]^{2+}$, and $[Co(etolen)_2]^+$ in different proportions, depending on the Co/etolenH ratio and the resulting pH. In some cases, dark red-brown oils, extremely soluble in both water and ethanol, were obtained, but no product of any definite composition could be isolated from such oils by treatment with other solvents, or by precipitation as the tetraphenylborate or the hexanitrocobaltate(III). The reaction of etolenH with $(Co(NH_3)_6]^{3+}$ or with $[Co(NO_2)_6]^{3-}$ was extremely slow at room temperature in the absence of a catalyst. In the presence of activated carbon, the former gave $[Co(etolenH)(etolen)]^{2+}$ or $[Co(etolen)_2]^+$ or a mixture thereof, while the latter gave $[Co(etolenH)(NO_2)_4]^-$, $[Co(etolenH)_2(NO_2)_2]^+$, and some $[Co(etolen)_2]^+$.

The methods of preparation and properties of etolenH complexes other than $[Co(etolen)_2]I$ will be communicated in a separate paper. Keller and Edwards observed the formation of this complex as a purple solution and Tennenhouse first isolated the complex iodide in the solid state. Tennenhouse's method, as modified in the present study, is given below.

N-Hydroxyethylethylenediamine was obtained from Matheson Coleman and Bell and used without further purification. The equivalent weight, as obtained by potentiometric titration, was found to be 52.4 (theoretical 52.1) when freshly opened. *Anal.* Calcd for $C_4H_{12}N_2O$: C, 46.15; H, 11.54; N, 26.92. Found: C, 46.26; H, 11.74; N, 27.12.

Hexaamminecobalt(III) iodide was prepared by the action of potassium iodide solution on a saturated solution of hexaamminecobalt(III) chloride.[6]

Bis(hydroxyethylethylenediamine)cobalt(III) iodide was prepared by mixing 27 g of hexaamminecobalt(III) iodide (0.05 mole) intimately with 2 g of activated carbon (Aqua Neuchar A, West Virginia Pulp and Paper Co.). To this was added 100 ml of a 1 *M* solution of etolenH (0.1 mole) followed by 4 g of sodium hydroxide dissolved in 25 ml of water. This mixture was heated on the steam bath until all of the ammonia was expelled. About 50 ml of water was added and the mixture was heated on the steam bath to dissolve the deep purple product which had formed. The solution was filtered to remove carbon and the filtrate was concentrated to about 30 ml and then cooled in ice. Ethanol was added to precipitate the purple crystals of the complex iodide. These were filtered and washed twice with methanol, and then with absolute ethanol. The product was dried in an oven at 105°, yield 14 g (72%). Larger crystals may be obtained by slowly recrystallizing from 80% methanol. The complex iodide is freely soluble in water, only slightly soluble in methanol, and insoluble (when completely dry) in ethanol, acetone, chloroform, and dimethyl sulfoxide. *Anal.* Calcd for $[Co(C_8H_{22}N_4O_2)]I$: C, 24.49; H, 5.61; N, 14.29; I, 32.40. Found: C, 24.69; H, 5.82; N, 13.96; I, 32.44.

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[5] The formulations given are based on analysis, molar conductance, and visible, uv, ir, and nmr spectra of these compounds. Most of these can exist in more than one stereoisomeric form.

[6] J. Bjerrum and J. P. McReynolds, *Inorg. Syn.*, **2**, 217 (1946).

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Infrared Evidence for Single Hydrogen Bridges in Boron Compounds

Sir:

The topic of single hydrogen bridges in certain diborane derivatives has been the subject of several recent communications,[1-3] and some doubt has been expressed whether this structural feature is actually present in the compounds in which it has been suggested. To date, the only physical evidence advanced has been that from nuclear magnetic resonance spectra, the bulk of the arguments being chemical in nature based on stoichiometry and thermodynamics. Although the available evidence strongly favors the existence of single hydrogen bridges, additional supporting results of a physical nature clearly appear desirable.

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[1] S. G. Shore and C. L. Hall, *J. Am. Chem. Soc.*, **88**, 5346 (1966).

[2] J. F. Eastham, *ibid.*, **89**, 2237 (1967).

[3] S. G. Shore and C. L. Hall, *ibid.*, **89**, 3947 (1967).