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Cobaltous Complexes of Cyclic Polyethers

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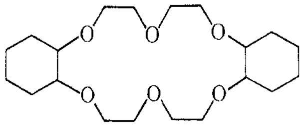
Pedersen[1] has recently reported the synthesis of a series of macrocyclic polyethers containing from 9 to 60 atoms with 3 to 20 oxygen atoms in the ring. Two outstanding examples are: an aromatic compound derived from catechol, 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene (I) and its hydrogenation product, a mixture of *cis–trans* isomers, 2,4,8,15,18,21-hexaoxatricyclo[20.4.0^{9,14}]hexacosane (II).



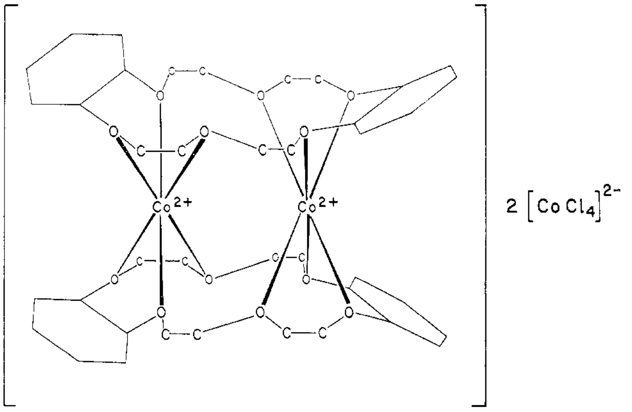
I, C_6 ring is aromatic
II, C_6 ring is saturated
III, II·2$CoCl_2$

The compounds were found, by Pedersen, to interact readily with alkali and alkaline earth metal cations to form relatively stable complexes.

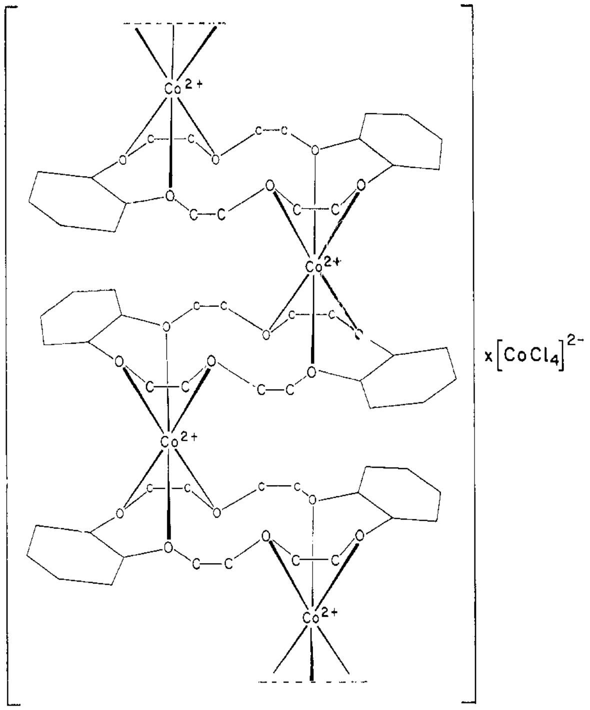
We have extended Pedersen's work by studying interactions of these compounds with a number of transition metal cations mainly within the first series. Complex formation between the cyclic ethers and metal cations such as Ti^{3+}, V^{3+}, Fe^{3+}, Co^{2+}, and Zn^{2+} has been observed in organic solvents of low dielectric constants, ϵ 2–9. The complex formation can be observed by change of colors, change of solubility, or spectral changes of the reactants. Among the above complexes, the one derived from $CoCl_2$ and II, *i.e.*, III, can be isolated most readily and we have studied this in some detail. This is the only complex that we wish to report in this note.

III is prepared by mixing a concentrated solution of II in acetic acid with a 0.2–0.5 *M* solution of $CoCl_2$ in acetic acid. The resulting blue solution was allowed to sit at room temperature in the absence of oxygen and moisture for a few days. The complex precipitated as blue crystals (approximately 90% yield based on II). It is interesting to note that, irrespective of the ratio of the reactants, the major product is always III. The best result for the preparation of III is obtained with a Co to cyclic ether ratio of 3. Complex III melts sharply at 238–239°. *Anal.* Calcd for $C_{20}H_{36}O_6Co_2Cl_4$: C, 38.0; H, 5.9; Cl, 22.5; Co, 18.7. Found: C, 38.0; H, 5.7; Cl, 22.5; Co, 18.9. III is insoluble in nonpolar solvents. In more polar solvents such as nitromethane, the complex tends to dissociate into the original components.

Based on the following spectral and magnetic data and with the help of a set of molecular models two probable structures, IV and V, can be drawn for complex III. The cationic moiety of IV involves a sandwich-type structure with two Co^{2+} squeezed between two cyclic ethers. In structure V the cationic moiety involves a polymeric structure with alternating array of cobalt cations and the cyclic ethers II. In both IV and V each cyclic ether contributes three oxygen atoms to each cobalt cation to form an octahedral complex.



IV



V

The spectrum of III in the visible region (taken *via* reflectance technique from a solid sample using $MgCO_3$ as reference) shows λ_{max} at 680 and 600 mμ. Its spectrum in the far-infrared region shows two doublet-type bands, one at 250 and 265 cm^{-1} and the other at 305 and 335 cm^{-1}. Comparison of the above spectral data with those given in the literature[2,3] points to the existence of the $CoCl_4^{2-}$ anion. The characteristic blue color of the complex also agrees with the presence of this anion.

The structure of the cationic moiety of complex III is also of interest since it may represent one of the weak-

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(1) C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 2495 (1967).

(2) R. J. H. Clark and T. M. Dunn, *J. Chem. Soc.*, 1198 (1963).

(3) N. S. Gill and R. S. Nyholm, *ibid.*, 3997 (1959).

est ligands bonded to the Co^{2+} cation. This was clarified to some extent based on a magnetic susceptibility study of complex III. Magnetic susceptibility of III was measured at 297, 78, and 4.2°K. The observed gram-atom susceptibility χ_M independent of magnetic field from 3000 to 8000 Oe was found to obey the Curie–Weiss relationship, $\chi_{Co} = C/(T - \theta)$, between 78 and 300°K. A Curie constant (C) of 2.86 ± 0.03 and a Weiss constant (θ) of -12 ± 2°K was obtained at 8000 Oe. The average magnetic moment per cobalt atom in complex III, $\bar{\mu}$, calculated from the equation $\bar{\mu} = \sqrt{3KC/N\beta^2}$ is equal to 4.78 ± 0.03 BM. The magnetic moment for the $CoCl_4^{2-}$ moiety based on the reported measurement[4] of Cs_2CoCl_4 is $\mu = 4.46$ BM. The moment for the moiety $[II \cdot Co^{2+}]$ can be calculated *via* the relationship $\bar{\mu}^2 = (\mu_1^2 + \mu_2^2)/2$ and was found to be 5.04 ± 0.04 BM. This value is very close to the value of 5.2 BM which is the moment exhibited by Co^{2+} in a high-spin octahedral complex ($^4T_{1g}$) with a spin–orbit coupling constant of $\lambda = 170\ cm^{-1}$.[5]

The fact that the above-calculated value of 5.04 BM is slightly lower than the expected value is not unreasonable for a complex such as $[II \cdot Co^{2+}]$ which is expected to depart at least to some extent from pure octahedral symmetry. Lowering of the moment toward the spin-only moment value is not uncommon for complexes in which the ligand field departs from perfect symmetry.

[4] A. Bose, *Indian J. Phys.*, **22**, 276 (1948).

[5] B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 185 (1964).

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Tributyltin Hydride Reduction of Chloroboranes

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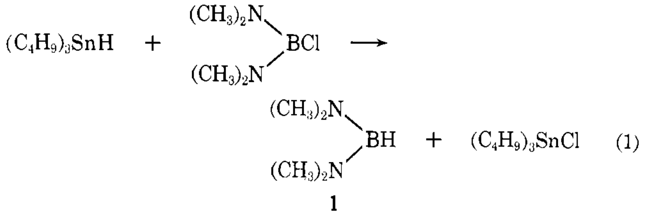
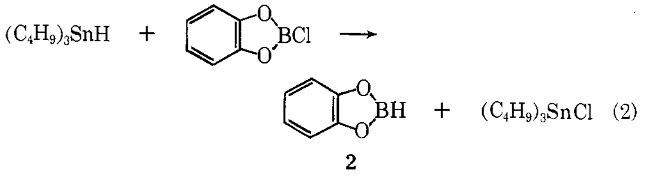
The majority of reductions by organotin hydrides proceed by free-radical mechanisms.[1] However, polar reactions have recently been established for the addition of organotin hydrides to phenyl and hexyl isocyanates,[2] for the cleavage of tin–nitrogen bonds by triphenyltin hydrides,[3] and for addition of tin hydrides to substituted acetylenes.[4] We wish to report convenient laboratory syntheses for bis(dimethylamino)borane (1) and 1,3,2-benzodioxaborole (2) by reduction of the corresponding B-chloro compound with tributyltin hydride and an investigation of the reaction mechanism.

Tributyltin hydride was found to react smoothly (neat) with bis(dimethylamino)chloroborane at 90° to give bis(dimethylamino)borane (1) in 73% yield. 2-Chloro-1,3,2-benzodioxaborole gave the corresponding hydride (2) in 42% yield. Infrared spectra suggested that tributyltin chloride also was produced in these reactions, in addition to other unidentified by-products.



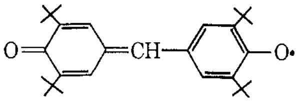
(1)



(2)

Reduction of alkyl halides by organotin hydrides has been demonstrated[1] to follow a free-radical path. More pertinent to reaction 1 is the fact that acid chlorides also react with organotin hydrides by a radical mechanism.[1] The electronic similarity between a chloroborane and an acid chloride might suggest a radical-chain mechanism for reaction 1 also.

If such a process did occur, the rate of the reaction should be enhanced by free-radical initiators and depressed by inhibitors. A polar mechanism should show no rate effect from these additives and should proceed faster in a polar solvent than in a nonpolar solvent. The reaction was carried out neat, with added α,α'-azobis(isobutyronitrile) (AIBN), with added galvinoxyl (3), and in hexane and chlorobenzene solvents.



3

Relative rates were obtained by measuring the increasing ratio of the B–H/Sn–H infrared absorptions periodically and plotting the ratio against time.

The results, listed in Table I, ruled out a radical-chain process and are consistent with a polar mechanism. The reaction was not catalyzed by added AIBN and was not inhibited by galvinoxyl. The effect of solvent was as expected for a bimolecular heterolytic reaction. In the nonpolar hexane (ϵ 1.87), the rate was greatly reduced by a dilution effect. In chlorobenzene (ϵ 5.9), dilution of reacting species again tended to reduce the rate but significant solvation stabilization of the polar transition state operated to increase the rate, with a net result of a rate close to that of the neat reactants. The moderate rate increase with added **3** could be due to its polarity.

The reaction appears to represent a fourth example of an organotin hydride reduction by a heterolytic mechanism, but the exact nature of the transition state is only speculative at this point. A four-centered

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[2] A. J. Leusink and J. G. Noltes, *Rec. Trav. Chim.*, **84**, 585 (1965).

[3] H. M. J. Creemers and J. G. Noltes, *ibid.*, **84**, 590 (1965).

[4] A. J. Leusink and J. W. Marsman, *ibid.*, **84**, 1123 (1965).