Reduction of *NN'*-Ethylenebis(salicylideneiminato)cobalt(II) and its Conversion into a Methyl Derivative Containing a Direct Cobalt–Carbon Bond

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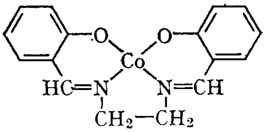
Two recent papers on organometallic compounds derived from bis(dimethylglyoximato)cobalt(II)[1] and *NN'*-ethylenebis(acetylacetoneiminato)cobalt(II)[2] prompted us to report our own results on the isolation of an organometallic compound derived from *NN'*-ethylenebis(salicylideneiminato)cobalt (II), hereinafter abbreviated as CoSaEn (I).



(I)

We have recently reported[3] on the preparation of oxygen complexes of (I) in solution and we were interested in the more general problem of possible relationships between oxygen complex formation on one side and stereochemistry or oxidation state of the central metal atom on the other side.

We have now found that the red CoSaEn (I) in which the central cobalt atom is in a d^7 low-spin configuration can be reduced, in tetrahydrofuran with sodium sand, to give green solutions containing the sodium salt Na[CoSaEn](II). The latter was isolated from the green solutions as a violet-black solid extremely sensitive to air. The reduced CoSaEn is a powerful nucleophilic reagent, it reacts readily with a number of substances containing electrophilic centres, such as water, and methyl iodide. By the latter reaction a methyl derivative was formed and isolated as the red-orange compound, MeCoSaEn,H_2O (III), by addition of water to the reaction mixture. On recrystallization from pyridine–heptane, (III) was converted into the red MeCoSaEn,pyridine (IV). The methyl derivatives (III) and (IV) give proton resonance spectra consistent with their proposed formulation, the methyl protons absorbing at τ 7·86 and 7·78, respectively, in deuterated dimethyl sulphoxide. The corrected molar magnetic susceptibility of the methyl derivative MeCoSaEn,pyridine is $\chi_M = 22 \times 10^{-6}$ c.g.s.u. at 298°K and at a field strength of 10,400 oersted. This result, together with the sharpness of the peaks in the n.m.r. spectrum, shows that no unpaired spins are substantially present in the molecule. It is interesting to note that while the observed diamagnetism proves that the methyl group is attached to the cobalt, no decision can be taken from magnetic properties alone concerning the actual oxidation state of the central metal atom in these complexes. The methyl derivative MeCoSaEn,H_2O can be dehydrated *in vacuo* over P_2O_5 at room temperature to give the olive-green MeCoSaEn. In the Figure we report the electronic absorption spectra of the reduced CoSaEn, of the methyl derivative, MeCoSaEn,pyridine, and the starting CoSaEn in tetrahydrofuran solution.

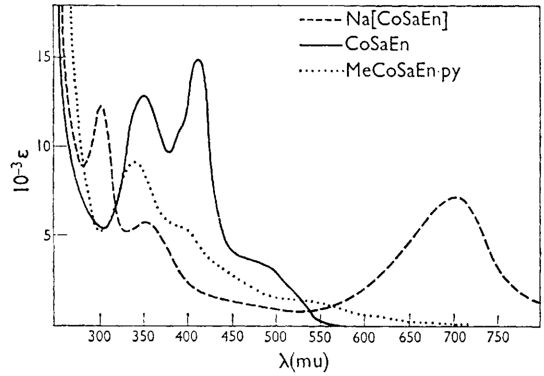


FIGURE. *Electronic absorption spectra.*

Reactions of the sodium derivative (II) with several other alkyl and acyl halides were also successfully carried out. The products from these reactions are now under investigation in order to determine the point of attachment of the alkyl or acyl group to the CoSaEn backbone.

Reductions of the porphirin[4] and phthalocyanine[5] systems and bis(dimethylglyoximato)cobalt(II)[6] are well established in the literature. The reduction of CoSaEn is, on the other hand, the first to be reported for a metal complex of a Schiff base, *i.e.*, a $Co^{II}–O_2N_2$ system.

Correct elemental analyses were obtained for the sodium derivative (II) and for all the other compounds reported in this Communication.

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