Oxidative Activation of Co^{II} in Schiff Base Complexes in the Presence of n-Butyltin Trichloride: the Molecular Structure of $Bu^nSn(OMe)Cl_2{\cdot}CoCl(salen)$ [salen = *N,N'*-ethylenebis(salicylideneaminato)]

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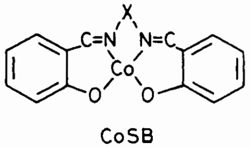
Air stable chloroform solutions of Schiff base complexes of Co^{II} undergo rapid cobalt oxidation on addition of n-butyltin trichloride yielding complexes in which, as exemplified by the crystal structure of $Bu^nSn(OMe)Cl_2{\cdot}CoCl$(salen) [salen = *N,N'*-ethylenebis(salicylideneaminato)], the cobalt(III) Schiff base species behave as Lewis bases towards tin(IV).

The ability of cobalt–Schiff base complexes to bind dioxygen, in many cases reversibly, is well known and has been the subject of many investigations.[1] A novel facet of cobalt activation in these complexes towards dioxygen uptake and other oxidative processes cames to light when we attempted the preparation of adducts of the type, $Bu^nSnCl_3{\cdot}CoSB$ (SB = Schiff base, see Figure 1). The reactivity of the Schiff base complexes in the presence of n-butyltin trichloride is summarized in Scheme 1.

The 1:1 addition complexes $Bu^nSnCl_3{\cdot}CoSB$ initially formed under oxygen free conditions have, in all probability, similar adduct type structures to those of $Me_2SnCl_2{\cdot}Ni(salen)$[2] and $CuCl_2{\cdot}Cu(salen)$[3] [salen = *N,N'*-ethylenebis(salicylideneaminato)] in which the oxygen atoms of the cobalt–Schiff base complexes form donor bonds to tin. Chloroform solutions of these adducts are surprisingly sensitive to oxygen attack and in the presence of dry oxygen rapidly yield dark brown solids. The diamagnetic nature of these solids coupled with elemental analytical data and dioxygen uptake measurements suggest that both cobalt and ligand oxidation is occurring in these reactions. However, when exposed to the atmosphere, solutions of the adducts rapidly yield the green diamagnetic hydroxy complexes $Bu^nSn(OH)Cl_2{\cdot}CoClSB$, which in methanol are readily converted into the methoxy complexes $Bu^nSn(OMe)Cl_2{\cdot}CoClSB$. An *X*-ray crystallographic study[†] of $Bu^nSn(OMe)Cl_2{\cdot}CoCl$(salen) (see Figure 2) confirmed its donor–acceptor nature

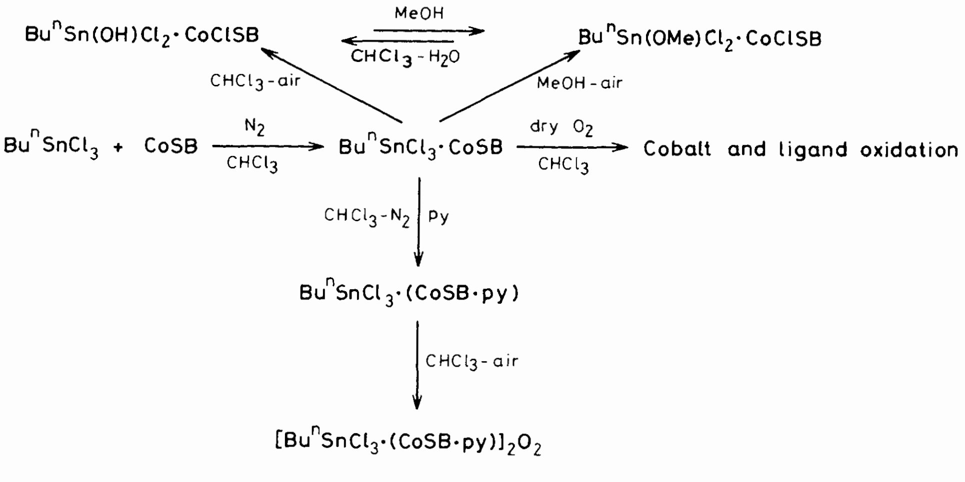


CoSB

X = ethylene, 1,2-propylene, *o*-phenylene, 3-methyl-*o*-phenylene

Figure 1

[†] *Crystal data:* Monoclinic, non-standard space group $B2_1/a$, $a = 22.412(5)$, $b = 10.850(3)$, $c = 22.781(6)$ Å, $\beta = 70.31°$; $U = 5212.52$ Å^3, $Z = 8$, $\mu(\text{Mo-}K_\alpha) = 17.98\ cm^{-1}$, $\lambda = 0.71073$ Å; crystal dimensions $0.5 \times 0.4 \times 0.4\ mm^3$. Tin and cobalt atoms were located by direct methods and structure refinement was by least squares techniques leading to $R = 0.047$ and $R_w = 0.060$ for 1546 reflections with $I > 3\sigma(I)$ collected at room temperature on a Hilger & Watts Y290 diffractometer. Goodness of fit = 1.585. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemistry Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



Scheme 1

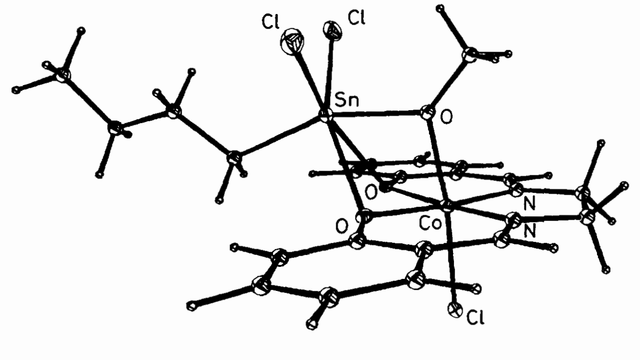


Figure 2. The structure of $\mathrm{Bu^nSn(OMe)Cl_2{\cdot}CoCl(salen)}$. Selected dimensions: Sn–C 2.173(11), Sn–Cl 2.392(3) and 2.474(3), Sn–OMe 2.090(8), Sn–O 2.410(6) and 2.300(6), Co–Cl 2.225(3), Co–OMe 1.923(8), Co–O 1.901(6) and 1.982(6), Co–N 1.937(9) and 1.861(9) Å. The salicylideneaminato ligand shows a slight umbrella distortion away from the methoxy group with the phenyl ring planes making angles of 4 and 4.7° to the least squares plane defining the oxygen and nitrogen atoms. Co is 0.073 Å from the least squares plane away from the methoxy group.

and the fact that the methoxy group is directly attached to tin providing at the same time a strong bridging oxygen donor bond to cobalt. We assume that this is the mode of bonding of methoxy and hydroxy groups in the other complexes. Nonetheless, it is virtually certain that oxidation of cobalt leads initially to the formation of cobalt–methoxy‡ and –hydroxy bonds (in methanol and chloroform respectively) after which exchange takes place with chloride on tin. Consistent with this is the fact that the adducts $\mathrm{Bu^nSnCl_3{\cdot}MSB}$ (M = Cu or Ni) do not form methoxy or hydroxy species under similar conditions.

Chloroform solutions of the pyridine (py) adducts $\mathrm{Bu^nSnCl_3{\cdot}(CoSB{\cdot}py)}$§ are also oxygen sensitive, in these instances behaving similarly under dried and undried oxygen conditions. In these reactions 0.5 mol dioxygen per mol of cobalt are irreversibly absorbed thus resulting in the formation of black microcrystalline solids. The black colour and diamagnetic nature of the products[1] coupled with dioxygen uptake measurements and elemental analytical data suggest that the μ-peroxo complexes $\mathrm{[Bu^nSnCl_3{\cdot}(CoSB{\cdot}py)]_2O_2}$ are the products of the reactions.

The oxidations described demonstrate that the reactivity of cobalt in the CoSB complexes is dramatically altered by the presence of the tin(IV) Lewis acid. For example, chloroform solutions of the Schiff base complexes are stable under ambient conditions and furthermore the μ-peroxo complexes $\mathrm{(CoSB{\cdot}py)_2O_2}$ liberate dioxygen in chloroform.[4] It is also noteworthy that only certain Lewis acids effectively alter the cobalt oxidation equilibrium. Thus, while dialkyltin dihalides¶ and n-butyltin trichloride rapidly promote cobalt oxidation neither the weaker Lewis acids $\mathrm{R_3SnCl}$ (R = Ph or alkyl), which do not form adducts with CoSB, nor the stronger Lewis acids $\mathrm{PhSnCl_3}$ and $\mathrm{SnCl_4}$, which form 1 : 1 adducts with CoSB, have the same effect. It has also been shown that cobalt oxidation does not occur in the presence of dimethyldichlorosilane.[5] The activating role of n-butyltin trichloride in promoting dioxygen uptake is extremely significant and may possibly be utilized in the design of new synthetic dioxygen carrying systems.

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References

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‡ The existence of Co(OMe)(salen) in methanolic solutions of Co(salen) exposed to oxygen has been invoked; it has not been isolated (G. Costa, G. Mestroni, and G. Pellizer, *J. Organometal. Chem.*, 1968, **15**, 187).

§ Electronic spectra indicate that pyridine is bonded to cobalt.

¶ Reactions involving dialkyltin dihalides rapidly yield diamagnetic materials which have not been characterized. On the basis of the available data it would appear that both cobalt and ligand oxidation is occurring.