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N,N'-ETHYLENEBIS(SALICYLIDENEIMINATO)COBALT(II). REDUCTION, OXIDATION AND CONVERSION INTO ALKYL AND ACYL DERIVATIVES

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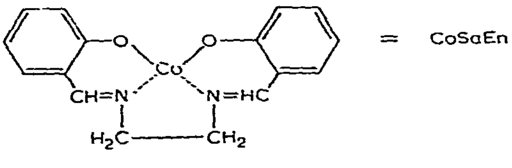
SUMMARY

Several reactions of *N,N'*-ethylenebis(salicylideneiminato)cobalt(II), CoSaEn, are reported. By reduction with sodium, the corresponding monoanion and the dianion have been isolated as the sodium derivatives. Oxidation of CoSaEn occurs very readily with formation of the iodo derivative in very good yield. The monosodium derivative is a strong nucleophilic reagent and reacts with a number of alkyl halides and with acetyl chloride to give derivatives of the type RCoSaEn or RCoSaEn·B where R is CH_3, C_2H_5, $(CH_3)_2CH$, n-C_4H_9, $C_6H_5CH_2$, C_6H_5, CH_3CO and B is H_2O or C_5H_5N. Some of the alkyl compounds have also been prepared by the Grignard method from [CoSaEn]I. Chemical evidence shows the direct attachment of the alkyl group to cobalt. The magnetic susceptibilities of the monosodium and iodo derivatives have been measured between 90°K and room temperature. The ^{59}Co nuclear magnetic resonances for some of the organometallic derivatives suggest that these compounds should better be regarded as cobalt(III) derivatives bonded to a carbanion.

INTRODUCTION

We have recently reported[1] the reduction of *N,N'*-ethylenebis(salicylideneiminato)cobalt(II), hereinafter abbreviated as CoSaEn, to a monoanion isolated as its sodium derivative Na[CoSaEn]. The existence of the monoanion which we obtained by sodium reduction of CoSaEn itself, has been later confirmed by Costa and Maestroni[2].



(A)

CoSaEn is a low-spin system of d^7 configuration and as such it can be regarded as a long-lived radical and its reactivity should therefore conform to this view[3]. CoSaEn appears to follow this general pattern of reactivity: it reacts in fact with oxygen either in solution[4] or in the solid state[5] and with nitrogen oxide[6]. It appeared therefore very interesting to investigate further its reactivity.

We have now carried out the reduction of CoSaEn by other methods and studied the reactivity of the $[CoSaEn]^-$ anion towards electrophilic reagents, in particular organic halides to obtain organometallic derivatives. The behaviour of CoSaEn towards mild oxidizing agents has been also investigated and the iodo cobalt(III) derivative [CoSaEn]I prepared. Although alkyl and acyl derivatives of Schiff bases metal complexes were unknown at the beginning of this work, they were recently prepared[7] by Grignard reactions on certain halo derivatives of hexacoordinated cobalt(III). The availability of the iodo derivative [CoSaEn]I made it possible to carry out Grignard reactions on a simple cobalt(III) species not containing other ligands except the Schiff base and the halogen, thus avoiding side reactions on the extra ligands around the cobalt. The results of the Grignard reactions on [CoSaEn]I are therefore directly comparable with those obtained by the new method[1,2] for preparing organometallic derivatives of CoSaEn, which consists of treating the $[CoSaEn]^-$ with organic halides.

EXPERIMENTAL

All of the operations for preparing the cobalt complexes reported in Table 1 were carried out under an atmosphere of nitrogen, especially during the reduction of CoSaEn and the isolation of the air-sensitive reduced species. The solutions of the organometallic derivatives were kept in an atmosphere of nitrogen and under exclusion of light. Tetrahydrofuran was distilled over sodium and lithium tetrahydridoaluminate and then stored under nitrogen. CoSaEn was prepared under nitrogen from anhydrous cobalt acetate and the Schiff base in dimethylformamide. Sodium sand was prepared by vigorous shaking of molten sodium in xylene previously distilled over sodium. The sand was then separated from xylene by filtration under dry nitrogen, dried in high vacuum and kept in vials sealed under dry nitrogen.

The molecular weights were measured with a Mechrolab vapour pressure osmometer model 301 A.

The magnetic susceptibilities were measured with a Gouy balance at different field strengths from 3200 to 11000 oe. The tube was filled with the sample in an atmosphere of nitrogen. The gram magnetic susceptibilities are estimated to be accurate to within 2%.

The infrared spectra were measured in mulls with a Perkin–Elmer 521 instrument.

Nuclear magnetic resonance spectra were measured with a Varian DP 60 A instrument.

1. *Reduction of CoSaEn with sodium*

(*a*) CoSaEn (4.35 g; 13.4 mmoles) was partially dissolved in 30 ml of tetrahydrofuran and treated at room temperature with sodium sand (0.3 g, 13.0 mg-at.). The initially orange-red solution became readily green; the reaction mixture was stirred vigorously until all the undissolved CoSaEn went into solution (about 3 h). At this point the green solution was filtered, concentrated and heptane was added until the sodium derivative separated out as a black-green crystalline solid, which was filtered

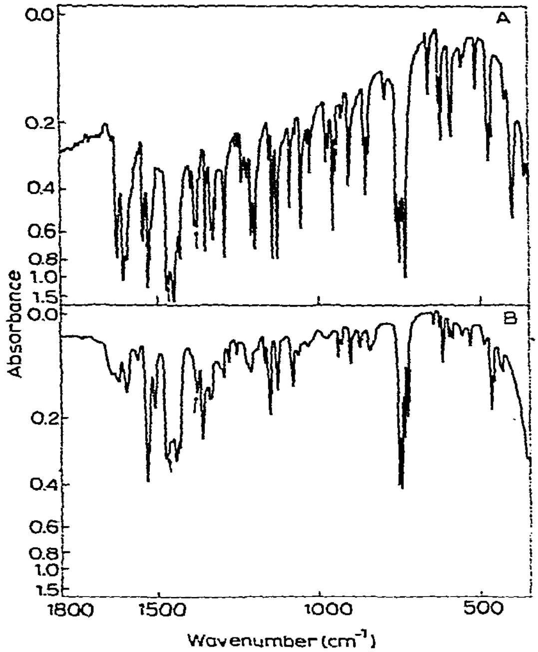


Fig. 1. Nujol mull spectra between 1800 and 400 cm^{-1} of CoSaEn (A) and its monosodium derivative (B). The arrows indicate absorptions due to nujol.

and dried *in vacuo* (3.65 g; 80.6% yield). The dry product is black violet, extremely sensitive to air and moisture.

The infrared spectrum of Na[CoSaEn] in comparison with that of CoSaEn is shown in Fig. 1.

The visible absorption spectrum of this compound has been reported in a previous publication[1].

(*b*) For the preparation of Na_2[CoSaEn], 5.1 g (15.7 mmoles) of CoSaEn was treated in tetrahydrofuran (50 ml) with two equivalents of sodium sand as previously described for the monosodium derivative, except that the reaction time was increased to 48 h. At the end of the reaction the green solution was filtered from a solid substance (probably undissolved disodium derivative) and heptane was added to the deep green filtered solution. The deep green substance so obtained was dried *in vacuo* (2.27 g; 39% yield).

In a control experiment no gas evolution was observed during the treatment of CoSaEn with sodium sand.

The disodium derivative is soluble in tetrahydrofuran, but less than the monosodium derivative, and very reactive even in the solid state against oxygen and moisture.

The analysis gave sodium and cobalt in the ratio 2.3. In order to prove the formulation of the product the following experiment was carried out. A tetrahydrofuran solution of the disodium derivative containing 165 mg of cobalt (0.44 mg-at) was rapidly added to a suspension of CoSaEn (125 mg; 0.38 mmoles) in tetrahydrofuran. During the time of addition (about 2–3 min) CoSaEn dissolved completely and a green solution of Na[CoSaEn] was obtained as a result of electron redistribution between $Na_2[CoSaEn]$ and CoSaEn:

$$Na_2[CoSaEn] + CoSaEn \rightarrow 2\,Na[CoSaEn] \tag{1}$$

2. *Further methods of reduction of CoSaEn*

(*a*) *With Grignard reagents.* To a suspension of CoSaEn (3.76 g; 11.56 mmoles) in tetrahydrofuran 11.53 mmoles of C_2H_5MgBr were slowly added under vigorous stirring at about 0°. This reaction was carried out in a three-necked flask connected with a mercury buret. By the end of the addition of the Grignard reagent (*ca.* 0.5 h) a green solution was obtained and gas was collected in the buret. The latter was examined by gas-chromatography and found to be constituted by ethylene and ethane. The green solution was filtered from some undissolved material (probably the magnesium derivative itself later described) and heptane was added to the solution. By filtration and drying *in vacuo* a green solid was isolated, which was identified as $[MgX]^+[CoSaEn]^-$ through its reaction with methyl iodide. The latter reaction was carried out in diethyl ether and $CH_3CoSaEn \cdot Py$ [compound (VI) in Table 1] was isolated, after treatment with H_2O, by recrystallisation from pyridine. The technique used for the isolation of compound (VI) is substantially identical to that used for the preparation of the same compound starting from solutions of Na[CoSaEn] (see *Section* 7).

The reduction of CoSaEn was repeated with CH_3MgI in diethyl ether obtaining similar results. The gases evolved during the reaction were found to be methane and ethane.

(*b*) *With lithium tetrahydridoborate.* CoSaEn (0.95 g; 2.92 mmoles) suspended in 20 ml tetrahydrofuran was treated under nitrogen with 0.190 g of lithium tetrahydridoborate (8.72 mmoles) at room temperature for 12 h. At the end of the reaction the green reaction mixture was filtered directly into a tetrahydrofuran solution of CH_3I. The methyl derivative (VI) was isolated as later described in 7.

3. *Preparation of N,N'-ethylenebis(salicylideneiminato)iodocobalt(III)*

CoSaEn (9.06 g; 27.9 mmoles) was treated with iodine (3.75 g; 14.8 mmoles) in 50 ml tetrahydrofuran for 6 h at room temperature under vigorous stirring. The black crystalline solid formed during the reaction was filtered, washed with tetrahydrofuran and dried *in vacuo* (11.85 g; 94% yield). The iodo derivative of CoSaEn is a black solid, slightly soluble in tetrahydrofuran.

4. *$CH_3CoSaEn \cdot H_2O$ (III)*

A tetrahydrofuran solution of the monosodium derivative (22.5 mmoles) prepared as described in 1 was filtered and slowly introduced into a tetrahydrofuran solution of methyl iodide maintained at about −80° under an atmosphere of nitrogen. A very fast reaction took place upon contact of the two solutions, as evidenced by an instantaneous change of color from green to red. The resulting tetrahydrofuran solution was allowed to warm up to room temperature and was then poured into water. The methyl derivative separated out, it was collected by filtration and dried *in vacuo*. Some of the properties of this compound have been already reported before[1,7]. It is stable in air in the solid state, but it is rather light-sensitive. The solubility of the compound in tetrahydrofuran is very small, it is more soluble in acetone and methanol. The NMR spectrum is reported in Table 3.

TABLE 1

PROPERTIES AND ANALYTICAL DATA OF SODIUM, ALKYL, ACYL AND IODO DERIVATIVES OF CoSaEn

Compound	Colour	Analysis, found (calcd.) (%)				Method of preparation[a]
		C	H	Co	N	
Na[CoSaEn]	Black-	54.82	4.21	16.55	7.96	
(I)	violet	(55.18)	(4.05)	(16.92)	(8.04)	
Na_2[CoSaEn]	Black-					
(II)[b]	green					
$CH_3CoSaEn \cdot H_2O$	Red-	57.14	5.31	16.63	8.70	*A*
(III)[c]	orange	(56.99)	(5.34)	(16.45)	(7.82)	
$CH_3CoSaEn$	Green	60.33	5.27	17.16		*A*
(IV)[c]		(60.05)	(5.03)	(17.33)		
$CH_3CoSaEn$	Red	59.89	5.05	17.20	8.13	*A*
(V)		(60.05)	(5.03)	(17.33)	(8.23)	
$CH_3CoSaEn \cdot Py$	Red-	62.98	5.28		10.23	*A*
(VI)[c]	orange	63.20	5.53	14.29	10.21	*B*
		62.74	5.46	14.28	10.24	*C*
		62.83	5.43	13.92	10.15	*D*
		63.05	5.28	13.93	10.18	*E*
		(62.96)	(5.28)	(14.05)	(10.02)	
$C_2H_5CoSaEn \cdot Py$	Red-	63.53	5.69	13.58	9.86	*F*
(VII)[c]	orange	(63.74)	(5.58)	(13.59)	(9.69)	
$(CH_3)_2CHCoSaEn \cdot Py$	Red	64.36	5.81	13.23	9.38	*A*
(VIII)		64.15	5.69	13.28	9.42	*F*
		(64.42)	(5.85)	(13.17)	(9.39)	
n-$C_4H_9CoSaEn \cdot Py$	Red-	65.68	6.13	12.19	9.03	*A*
(IX)[c]	orange	(65.07)	(6.11)	(12.77)	(9.10)	
$C_6H_5CH_2CoSaEn \cdot Py$	Orange-	67.85	5.21	11.90	8.61	*A*
(X)	yellow	(67.87)	(5.29)	(11.89)	(8.48)	
$C_6H_5CoSaEn \cdot Py$	Orange-			12.55	8.88	*F*
(XI)[c]	yellow			(12.24)	(8.72)	
$CH_3COCoSaEn \cdot Py$	Orange	61.48	5.02	13.35	9.39	*A*
(XII)		(61.74)	(4.95)	(13.17)	(9.39)	
[CoSaEn]I	Black	42.56	3.08	12.90	6.36	
(XIII)[d]		(42.50)	(3.12)	(13.03)	(6.19)	

[a] *A*: Na[CoSaEn]+RX → RCoSaEn;

B: $CoSaEn + CH_3MgX \rightarrow MgX[CoSaEn] \xrightarrow{CH_3I+Py} (VI)$;

C: $CH_3CoSaEn + Na \rightarrow Na[CoSaEn] \xrightarrow{CH_3I+Py} (VI)$;

D: $[CoSaEn]I + C_2H_5MgBr \rightarrow MgX[CoSaEn] \xrightarrow{CH_3I+Py} (VI)$;

E: $CoSaEn + LiBH_4 \rightarrow Li[CoSaEn] \xrightarrow{CH_3I+Py} (VI)$;

F: [CoSaEn]I+RMgX → RCoSaEn.

[b] Ratio Na/Co found 2.3. The compound could contain solvent of recrystallization. [c] Already reported in refs. 1, 2 and 7. [d] Analysis: I, found 28.21 %, calcd. 28.07 %.

Infrared spectrum (KBr disc): ~3400 (s, broad), 3050 w, 3020 w, 2925 m, 2900 w, 2855 w, 1620 vs, 1598 s, 1536 m, 1470 m, 1450 s, 1385 w, 1348 m, 1330 m–w, 1310 m, 1285 w, 1238 w, 1200 m, 1150 m, 1130 m, 1085 w, 1055 w, 1030 w, 952 w, 905 m, 850 w, 795 w, 755 m–s, 740 m, 662 w, 625 w, 598 w, 522 w, 472 w, and 430 w cm^{-1}.

5. *Green* $CH_3CoSaEn$ *(IV)*

This compound was obtained by dehydration of the aquo derivative (III) over P_2O_5 *in vacuo* (*ca.* $5 \cdot 10^{-2}$ mm) for several days under exclusion of light. The anhydrous methyl derivative is a green substance, stable in dry air, but readily affected by light and by moisture which converts it back to the aquo derivative. The green methyl derivative gives a red solution in tetrahydrofuran. Its molecular weight in dichloromethane was found to be 318 (calcd. 340.3 for the monomer). The compound turns red even when kept in vials sealed under nitrogen under exclusion of light. Several weeks are necessary in order for this change of colour to become noticeable.

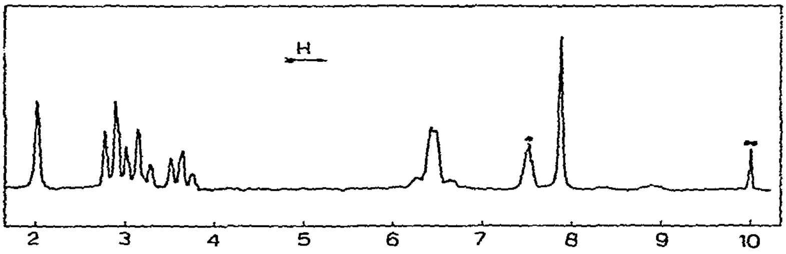


Fig. 2. Nuclear magnetic resonance spectrum of the methyl derivative (V) in dimethyl sulfoxide-d_6. The peaks labelled * and ** are due to partially deuterated solvent and to tetramethylsilane, respectively.

6. *Red* $CH_3CoSaEn$ *(V)*

The best method for obtaining this isomer of the anhydrous methyl derivative consists of treating the green compound (IV) with anhydrous diethyl ether. An immediate change of color took place and the red isomer was isolated by filtration and drying *in vacuo*. The NMR spectrum of this compound in dimethyl sulfoxide-d_6 is shown in Fig. 2.

7. $CH_3CoSaEn \cdot Py$ *(VI)*

The green anhydrous methyl derivative (IV) (1.72 g; 5.05 mmoles) was suspended under nitrogen in anhydrous pyridine (20 ml) at room temperature. By addition of heptane (100 ml) the solubility of the cobalt complex was considerably decreased. The product was filtered and dried *in vacuo* (1.34 g; 63.3% yield). This compound is diamagnetic, as indicated in Table 2.

The methyl derivative (VI) was also prepared by a similar procedure starting from the aquo derivative (III).

Infrared spectrum (KBr disc): 3075 w, 3058 m, 3020 w, 3010 w, 2960 w, 2890 m, 2853 w, 1615 vs, 1595 s, 1527 s, 1461 s, 1452 vs, 1444 s, 1430 m, 1400 w, 1382 m, 1344 s, 1328 m–s, 1318 m–s, 1238 m, 1220 w, 1193 s–m, 1140 s–m, 1122 m, 1081 m, 1071 m, 1050 m–w, 1037 w, 1027 m, 1007 m, 975 w, 950 m, 900 m–s, 848 m, 765 m, 748 s, 738 s, 702 m–s, 660 w, 621 m, 592 w, 512 w, 468 m–w, 435 w, and 412 w cm^{-1}.

8. $RCoSaEn \cdot Py$ *(VIII), (IX), (X), (XII)*

These compounds were all obtained by the same procedure. They were prepared from green tetrahydrofuran solutions of the monosodium derivative by treatment with alkyl or acetyl halides. We report here the method used in the case of compound (VIII).

A green tetrahydrofuran solution (50 ml) prepared according to (1*a*) and containing 12.0 mmoles of the monosodium derivative was introduced slowly into a solution of isopropyl chloride (3.44 g; 43.8 mmoles) in tetrahydrofuran (50 ml) at −80°. After 0.5 h the reaction mixture was allowed to warm up to room temperature during 1 h and pyridine (5 ml) was added. After one additional hour, the red solution was filtered and reduced to half its volume *in vacuo*. By addition of heptane the isopropyl derivative precipitated out as red brown crystals. These were filtered and dried *in vacuo* (3.1 g; 57.7% yield).

Infrared spectrum of the acetyl derivative (XII) as nujol mull: 1698 vs, 1620 s, 1610 s, 1590 m–s, 1527 m, 1520 m–s, 1452 vs, 1440 s, 1348 m–s, 1329 w, 1322 m–w, 1240 m–w, 1218 w, 1196 m, 1145 m, 1128 m–w, 1083 m–w, 1078 m, 1054 m–w, 1038 w, 1028 w, 1000 w, 972 w, 952 w, 943 w, 902 m, 855 w, 845 w, 790 w, 750 s, 743 m, 701 m–s, 662 w, 622 w, 618 m–w, 595 w, 574 m–w, 522 w, 515 w, 469 m–w and 428 w cm^{-1}.

9. *Preparation of alkyl derivatives by the Grignard method*

We report in detail the preparation of compound (VII), the procedure being the same for compounds (VIII) and (XI).

For a successful preparation of the alkyl derivatives by this method it was essential not to exceed the amount of Grignard reagent above the stoichiometric amount in order to avoid the further reduction of the intermediate alkyl with the Grignard reagent (see also *section* 10*a*).

The iodo derivative [CoSaEn]I (1.36 g; 3.0 mmoles) was suspended under nitrogen in 10 ml tetrahydrofuran and the ethyl Grignard reagent (3.0 mmoles of a 0.13 *M* solution) prepared from C_2H_5Br and magnesium in tetrahydrofuran was added very slowly to the stirred suspension maintained at about −10°. The resulting red solution of the ethyl derivative was allowed to warm to room temperature overnight and then poured into cold water. The cobalt complex was filtered, dried *in vacuo* over P_2O_5 for several days and then recrystallised from pyridine/heptane as described in 7 (34% yield).

We also report the preparation of the methyl derivative (VI) obtained from [CoSaEn]I. This exemplifies this type of reaction when a large excess of the Grignard reagent is used.

The iodo derivative [CoSaEn]I (0.98 g; 2.17 mmoles) was suspended under nitrogen in 40 ml tetrahydrofuran and 8.6 mmoles of C_2H_5MgBr in tetrahydrofuran were slowly added at about −10°. A red colour appeared at the beginning of the addition of the Grignard reagent. After the first equivalent was added, a green colour became evident and evolution of ethane and ethylene was observed. The final mixture was allowed to warm to room temperature, treated with methyl iodide and the resulting $CH_3CoSaEn$ isolated as $CH_3CoSaEn\cdot Py$ as described in 7 (33% yield).

10. *Proof of structure for the alkyl and acyl derivatives*

We report here in detail the investigation of chemical reactivity carried out on the methyl derivative aimed to establishing the bonding of the alkyl group to cobalt. One or more of these reactions were successfully carried out on the other compounds of the same series, as indicated below.

(*a*) The methyl derivative (IV) (0.83 g; 2.44 mmoles) suspended in diethyl ether (20 ml) was treated at about −10° under nitrogen with four equivalents of

CH_3MgI in the same solvent (30 ml). The originally red solid became gradually green, while evolution of gas (identified as methane and ethane) took place. The blue-green mixture so obtained was poured into cold water and 5 ml of 2 *N* HCl were added. The brown solid so precipitated was filtered, dried *in vacuo* over P_2O_5 for 3 h and recrystallised from pyridine/heptane. This compound was identified as CoSaEn·Py by infrared spectrum and analysis. These reactions can account for the observed facts.

$$CH_3CoSaEn + CH_3MgI \rightarrow 2\,\{CH_3^{\cdot}\} + MgI[CoSaEn] \tag{2}$$

$$MgI[CoSaEn] + H_2O \rightarrow Mg(OH)I + \{HCoSaEn\} \tag{3}$$

$$2\,\{H[CoSaEn]\} \rightarrow H_2 + 2\,CoSaEn \tag{4}$$

Hydrogen evolved during the reaction was identified by gas-chromatography.

(*b*) The operation described above was repeated in tetrahydrofuran with sodium sand, instead of CH_3MgI. Methane and ethane were detected by gas-chromatography. The formation of the sodium derivative was evidenced by its conversion into the methyl derivative (VI). The latter was characterized by elemental analysis and infrared spectrum.

(*c*) The green methyl derivative (IV) was irradiated with a mercury lamp in an atmosphere of hydrogen. No solvent was present. In the gas evolved during the irradiation, methane was detected by gas-chromatography.

(*d*) The methyl derivative (III) was heated at about 50° with 85% sulfuric acid. Gas evolution took place; the gas was shown by gas-chromatography to consist mainly of methane and carbon monoxide.

(*e*) A tetrahydrofuran suspension of (IV) (0.525 g; 1.54 mmoles) was treated with iodine (0.415 g; 1.63 mmoles) for 3 h at room temperature. At the end of reaction, the black precipitate of the iodo derivative [CoSaEn]I was filtered and dried (0.53 g; 77% yield).

The ethyl derivative (VII) gave ethane and ethylene by reduction with sodium. The isopropyl derivative (VIII) gave propane by reduction with sodium and the iodo derivative [CoSaEn]I in practically quantitative yields by treatment with iodine. Pyrolysis of the benzyl derivative (X) at 110–120° resulted in the formation of bibenzyl characterised by melting point and infrared spectrum. Traces of toluene were also detected by gas-chromatography. Finally, the treatment of the phenyl and acetyl derivatives (XI) and (XII) with iodine gave [CoSaEn]I in practically quantitative yields.

RESULTS AND DISCUSSION

Reduction and oxidation of CoSaEn

The present investigation shows that CoSaEn can be reduced chemically to the monoanion and also to the dianion depending on the reaction conditions. Although polarographic reductions of Schiff base complexes of copper[8] and cobalt[9] have appeared in the literature, our preliminary note[1] reported the first reduction of a cobalt complex of this type carried out chemically. We have found that longer reaction times and excess sodium cause the addition of a second electron to CoSaEn with formation of a dianion which we have also isolated as the disodium derivative. Because of its extreme sensitivity to air, conventional elemental analyses could not be obtained for this compound. On the other hand, the Na/Co ratio and the successful reduction of CoSaEn to Na[CoSaEn] by $Na_2[CoSaEn]$ definitely established the formulation as dianion.

The comparison of the infrared spectra of CoSaEn and of its monoanion (see Fig. 1 A and B) shows some interesting features. The bands of CoSaEn around 1600 cm^{-1} which have been attributed[10,11] to C=N stretching vibrations in similar metal systems, decrease in intensity or disappear completely upon introduction of an electron in the system. On the other hand the bands around 1500 cm^{-1} usually attributed to C=C stretching vibrations of the aromatic ring[10] are less affected. These findings can be explained in terms of delocalisation of the electron introduced in the system into the organic ligand, particularly into the C=N bond. This brings to the question of what is the charge of the central metal atom in the monoanion and in the dianion derivatives. To consider the extra electrons as completely localized on the central metal atom appears to be an oversimplification.

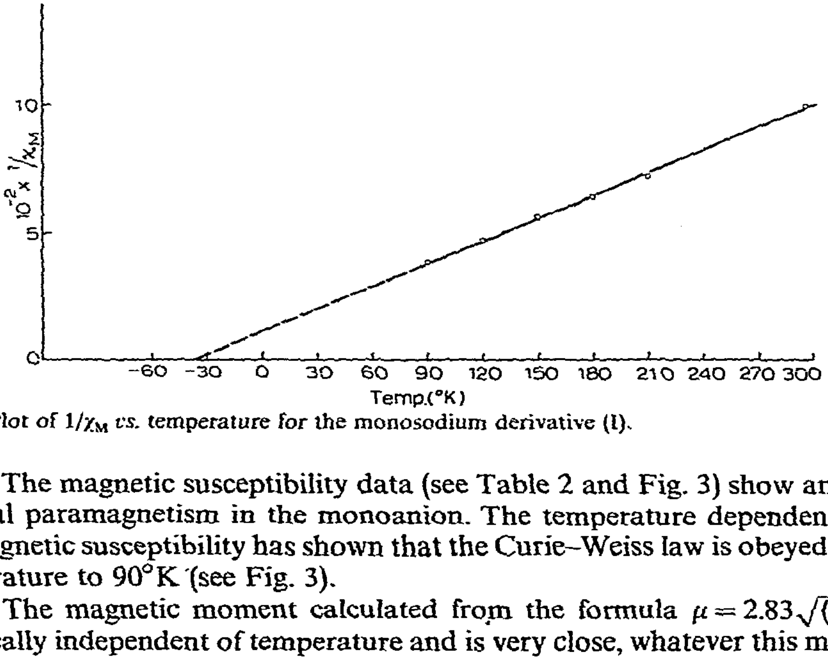


Fig. 3. Plot of $1/\chi_M$ *vs.* temperature for the monosodium derivative (I).

The magnetic susceptibility data (see Table 2 and Fig. 3) show an important residual paramagnetism in the monoanion. The temperature dependence study of the magnetic susceptibility has shown that the Curie–Weiss law is obeyed from room temperature to 90°K (see Fig. 3).

The magnetic moment calculated from the formula $\mu = 2.83\sqrt{(T+\theta)\chi_M}$ is practically independent of temperature and is very close, whatever this means, to the value for one unpaired electron. The magnetic results for the monosodium derivative are regarded as a further indication of considerable electron delocalisation in the organic ligand.

Other methods of reduction of CoSaEn have also been found. One of these is the reaction of CoSaEn with Grignard reagents:

$$\mathrm{CoSaEn} + \mathrm{CH_3MgBr} \rightarrow \{\mathrm{CH_3^{\cdot}}\} + \mathrm{MgBr^+[CoSaEn]^-} \qquad (5)$$

or with lithium tetrahydridoborate:

$$\mathrm{CoSaEn} + \mathrm{LiBH_4} \rightarrow \tfrac{1}{2}\,\mathrm{H_2} + \tfrac{1}{2}\,\mathrm{B_2H_6} + \mathrm{Li[CoSaEn]} \qquad (6)$$

The successful reduction of CoSaEn by lithium tetrahydridoborate contrasts with

TABLE 2

MAGNETIC DATA OF CoSaEn DERIVATIVES[a]

Compound	$10^6 \times \chi_M$ (c.g.s.u.)	Temp. (°K)	$10^6 \times$ diamagnetic correction per mole (c.g.s.u.)	θ	μ_{eff} (B.M.)	μ (B.M.)
Na[CoSaEn] (I)	2620	90	−182	+37°	1.37	1.63
	2129	120				
	1788	150				
	1551	180				
	1378	210				
	1000	296			1.54	1.63
$CH_3CoSaEn \cdot Py$ (VI)	53[b]	296	−240			
[CoSaEn]I (XIII)	179	90	−220			
	155	120				
	142	150				
	144	180				
	139	210				
	142	240				
	134	296				

[a] The μ(B.M.) is calculated by using the formula $\mu = 2.83\sqrt{\chi_M(T+\theta)}$. The magnetic susceptibilities χ_M contain the diamagnetic correction. [b] The same magnetic susceptibility was found, within the experimental error, on samples of this compound prepared either from the green methyl derivative (IV) or from the aquo derivative (III) by treatment with pyridine (see *experimental section*).

the reported[2] isolation of CoSaEn by treatment of cobalt(III) derivatives, for example $[(CoSaEn)(NH_3)_2]X$, with sodium tetrahydridoborate. Reaction conditions were, however, not specified.

A further interesting method of reduction of CoSaEn, although not practical from a preparative point of view, is the treatment of alkyl derivatives RCoSaEn with Grignard reagents. This type of reduction will be discussed in details later.

CoSaEn has also been found to react readily with iodine in tetrahydrofuran to give the iodo derivative [CoSaEn]I in excellent yields. The reaction takes place at room temperature and does not appear to be activated appreciable by visible or ultraviolet light.

[CoSaEn]I is diamagnetic. The values of χ_M are substantially independent of temperature in all the range investigated. The small positive magnetic susceptibility (see Table 2) experimentally found is therefore due to temperature independent paramagnetism, as shown by the plot of μ_{eff} against $\sqrt{T}$ (see Fig. 4). The small deviations from linearity observed in this graph are not regarded as significant in view of the lower degree of accuracy of the measurement in this particular case and to the small values of χ_M relative to the diamagnetic correction.

Alkyl and acyl derivatives of CoSaEn

Reduced CoSaEn behaves as a strong nucleophile and reacts very readily with

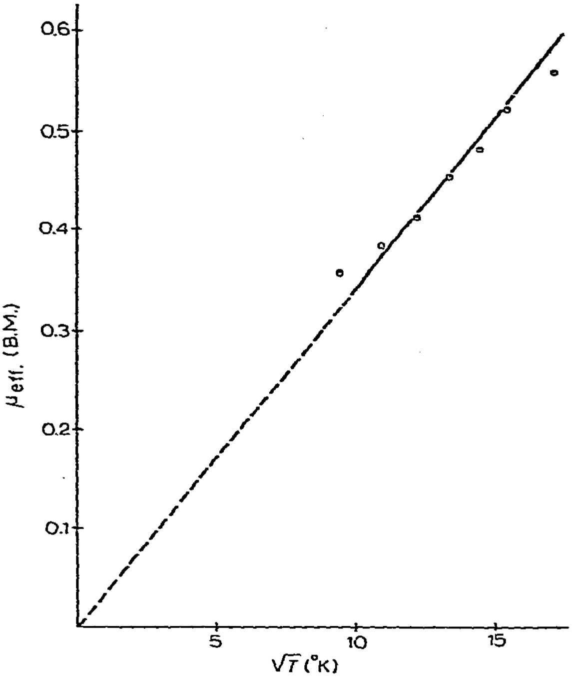


Fig. 4. Plot of μ_{eff} *vs.* $\sqrt{T}$ for the iodo derivative [CoSaEn]I (XIII).

alkyl halides and with acetyl chloride to give alkyl derivatives R[CoSaEn] and CH_3CO[CoSaEn], respectively.

$$\text{Na[CoSaEn]} + \text{RX} \rightarrow \text{R[CoSaEn]} + \text{NaX} \quad (7)$$

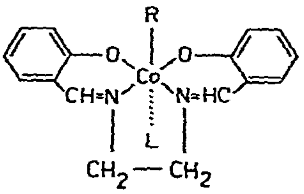
$$\text{Na[CoSaEn]} + CH_3COCl \rightarrow CH_3CO\text{[CoSaEn]} + \text{NaCl} \quad (8)$$

Some of the alkyl derivatives reported in Table 1, namely those with $R = C_2H_5$, $(CH_3)_2CH$ and C_6H_5, have been obtained by the Grignard method.

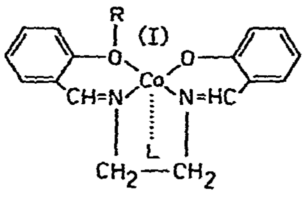
$$\text{[CoSaEn]I} + \text{RMgBr} \rightarrow \text{R[CoSaEn]} + \text{MgBrI} \quad (9)$$

The isopropyl derivative (VIII) has been prepared by both methods.

Although some of the alkyl derivatives have been already reported by Costa and coworkers[6], our analytical data are given in Table 1 and the preparative methods are described in the experimental section. This is because only preliminary accounts of alkylation and acetylation of Na[CoSaEn] have appeared[1,2] and also because our results on the Grignard reactions of [CoSaEn]I differ in some respects from those reported by Costa and coworkers[7]. The latter authors had used initially the Grignard method to prepare the alkyl derivatives of CoSaEn. However, since [CoSaEn]I was not available to them, they used cobalt(III) halogen compounds of formula [(CoSaEn)-L_2]X, in which L is NH_3, C_5H_5N, $C_6H_5CH_2NH_2$ or [(CoSaEn)(PPh_3)Br] as starting materials. Three equivalents of Grignard reagent were used by Costa and coworkers, whereas we find that if we use more than one equivalent of Grignard in the course of reaction (9) further reaction of the intermediate RCoSaEn takes place with formation of $[\text{CoSaEn}]^-$ [see *Sections* 9 and 10 and eqn. (2) in the experimental section], the alkyl group being lost as RH or RR. These apparently contradicting



(B)



(C)

facts can probably be explained by assuming that the amount of Grignard reagent was accidentally correct in Costa and coworkers' reaction due to consumption of two of the three equivalents by the ligands[12].

Magnetic and chemical evidence shows that (B) is the correct structure for the alkyl and acyl derivatives of CoSaEn, *i.e.* with a direct cobalt–carbon bond. Chemical evidence (formation of the hydrocarbon RH by treatment of RCoSaEn with sodium, formation of RH and RR by treatment with RMgBr, formation of [CoSaEn]I by reaction with iodine, pyrolysis of RCoSaEn to give RR) was necessary in order to exclude the alternative possibility of structure (C) containing a cobalt atom in oxidation state 1+ and therefore magnetically not distinguishable from formulation (B).

TABLE 3

PROTON MAGNETIC RESONANCE DATA OF ALKYL AND ACYL CoSaEn DERIVATIVES

Compound	Chemical shift[a] τ (ppm)	Multiplicity	Integrated area	Assignment
$CH_3CoSaEn \cdot H_2O$ (III)	1.98	Singlet	2	N=CH
	2.75–3.73	Complex pattern	8	C_6H_5
	6.43	Broad singlet	4	CH_2
	6.65	Singlet	2	H_2O
	7.86	Singlet	3	CH_3
$CH_3CoSaEn$ (V)[b]	2.03	Singlet	2	N=CH
	2.78–3.75	Complex pattern	8	C_6H_5
	6.42	Broad[c]	4	CH_2
	7.88	Singlet	3	CH_3
$CH_3CoSaEn \cdot Py$ (VI)	6.48	Broad singlet	4	CH_2
	7.78	Singlet	3	CH_3
$(CH_3)_2CHCoSaEn \cdot Py$ (VIII)	10.13	Asymmetric doublet		CH_3
n-$C_4H_9CoSaEn \cdot Py$ (IX)	6.45	Broad singlet	4	CH_2
	8.78–9.43	Complex pattern	9	n-C_4H_9
$C_6H_5CH_2CoSaEn \cdot Py$ (X)	5.48	Singlet	2	$CH_2C_6H_5$
	6.43–7.07	Complex pattern	4	CH_2
$CH_3COCoSaEn \cdot Py$ (XII)	6.40	Broad singlet	4	CH_2
	7.35	Singlet	3	CH_3CO

[a] From tetramethylsilane (τ 10 ppm) as internal reference. The solvent is dimethyl sulfoxide-d_6. [b] The methyl derivative (IV) gives an identical spectrum. [c] Approximates AB spectrum; the coupling constant *J* is approximately 10 cps.

The methyl derivative (IV) is a monomer in dichloromethane. Molecular weights of the other compounds were not measured but there are no reasons to suspect of their monomeric nature in solution.

The proton nuclear magnetic resonance data for some of the alkyl derivatives are indicated in Table 3. The resolution of the peaks was usually not very good.

The NMR spectrum of the methyl derivative (V) is reported in Fig. 2. The positions of the protons of the iminic and phenyl groups are in agreement with those reported for diamagnetic cobalt(III) complexes of *N*-substituted salicylaldimines[13]. The methylenic protons of the ethylene bridge are at about τ 6.42 ppm, position which is not affected by changes in the alkyl group or in the ligand *trans* to it. This peak is usually a broad singlet due to the proximity of nitrogen with its quadrupole moment. It is interesting to notice that the two hydrogens within each methylene group should not be equivalent because of their different orientation with respect to the axial positions, *i.e.* in the direction perpendicular to the $Co\text{-}O_2N_2$ plane.

An incipient non-equivalence of the methylene protons is observed in the case of compound (V).

The positions of the protons of the alkyl groups bonded to cobalt are worth commenting. The methyl protons absorb at about τ 7.8 ppm, which is 2.3 ppm lower than the absorption observed in $CH_3Mn(CO)_5$[14] and about 1.5 τ lower than the resonances observed for the methyl derivatives of the dimethylglyoximatocobalt system[15]. It is also interesting to notice that the methylene protons of the benzyl group in compound (X) absorb at τ 5.48 ppm, whereas the similar resonance[14] in $C_6H_5CH_2Mn(CO)_5$ is at about 7.6 ppm. On the other hand, the acetyl protons of $CH_3COMn(CO)_5$[14] and the acetyl derivative (XII) absorb almost at the same position, which is reasonable since the protons are in β position with respect to the metal.

An interesting problem connected with the existence of organometallic derivatives of CoSaEn is the charge distribution around the cobalt–carbon bond. The magnetic susceptibility measurement at room temperature on the methyl derivative (VI) has shown the compound to be diamagnetic (see Table 2), temperature-independent paramagnetism being probably responsible for the small positive susceptibility we have found. Preliminary magnetic data on some of the compounds *in the solid state* would tend to suggest that diamagnetism is perhaps not a general characteristic of this class of compounds and that changes in the alkyl group or in the axial ligand could cause a change of the magnetic properties, namely the appearance of a low-lying paramagnetic state. We can for the time being limit the discussion to the diamagnetic methyl derivative (VI) and to solutions of the compounds in coordinating solvents, in which diamagnetism is well established, as suggested by the reasonably sharp NMR peaks. Magnetic properties have been used to decide about the charge distribution around the cobalt–carbon bond for compounds of this class[2,7] and for the methyl cobalamin[16], these compounds being regarded usually as cobalt(III) derivatives with a carbanion ligand attached to it. We would like to point out that the magnetic properties and chemical reactivity alone cannot decide about charge distribution and some better criterion should be found. The two other possible configurations—namely $\mathrm{Co}^{\mathrm{I}(-)}\mathrm{R}^{(+)}$ and $\mathrm{Co}^{\mathrm{II}}\ldots\mathrm{R}$—could very well result in a fundamentally diamagnetic ground state. We have tried to answer this question by measuring the ^{59}Co resonance spectra of the methyl and acetyl derivatives of CoSaEn in comparison

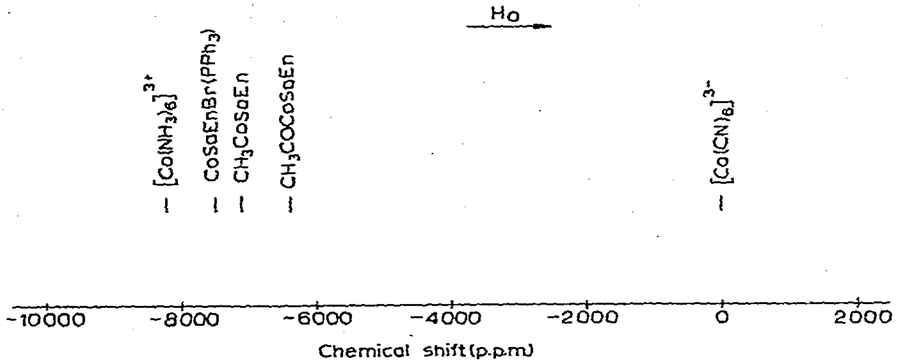


Fig. 5. ^{59}Cobalt nuclear magnetic resonance of CoSaEn derivatives.

TABLE 4

^{59}Co NUCLEAR MAGNETIC RESONANCE OF CoSaEn DERIVATIVES[a]

Compound	Chemical shift[b] (ppm)	Line width (gauss)
CoSaEnBr(PPh$_3$)	-7510 ± 150	50
CH$_3$CoSaEn	-7125 ± 15	5.6
CH$_3$COCoSaEn	-6400 ± 10	6.1

[a] Dimethylformamide solutions approximately 0.15 *M*. [b] From aqueous solution of K$_3$[Co(CN)$_6$].

with CoSaEn(PPh$_3$)Br[7] for which a cobalt(III) formulation is certainly the most appropriate. From the data of Table 4 and from the schematic representation of Fig. 5 it can be seen that the cobalt resonances for the methyl and acetyl derivatives are well within the range of normal cobalt(III) derivatives[17], and furthermore, very close to the bromo triphenylphosphine compound. These results suggest that the most reasonable formulation of the organometallic derivatives of CoSaEn is that which regards them as cobalt(III) derivatives.

Finally, it is interesting to notice that the formally pentacoordinate methyl derivative (IV) can be converted into its red isomer (V) simply by treatment with diethyl ether. The reasons for the difference in colours between these two compounds are not clearly understood. Possibly the red isomer is hexacoordinate, the sixth position around the cobalt being occupied by the oxygen atom of another chelate unit. The *N,N'*-ethylenebis(salicylideneiminato) complexes of iron[18] and copper[19] have actually been shown to be dimers of this type in the solid state.

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REFERENCES

1 F. Calderazzo and C. Floriani, *Chem. Commun.*, (1967) 139.
2 G. Costa and G. Mestroni, *Tetrahedron Lett.*, (1967) 1783.
3 J. Halpern, *Chem. Eng. News*, (1966) 68, Oct. 31.
4 F. Calderazzo, C. Floriani and J.-J. Salzmann, *Inorg. Nucl. Chem. Lett.*, 2 (1966) 379; and manuscript in preparation.
5 A. E. Martell and M. Calvin, *Chemistry of the Metal Chelate Compounds*, Prentice-Hall, Englewood Cliffs, N.J., 4th ed., 1959, p. 337.
6 A. Earnshaw, P. C. Hewlett and L. F. Larkworthy, *J. Chem. Soc.*, (1965) 4718.
7 G. Costa, G. Mestroni and L. Stefani, *J. Organometal. Chem.*, 7 (1967) 493.
8 M. Calvin and R. H. Bailes, *J. Amer. Chem. Soc.*, 68 (1946) 949.
9 J. R. Urwin and B. West, *J. Chem. Soc.*, (1952) 4727.
10 E. J. Olszewski and D. F. Martin, *J. Inorg. Nucl. Chem.*, 26 (1964) 1577.
11 P. Teyssie and J. J. Charette, *Spectrochim. Acta*, 19 (1963) 1407.
12 M. S. Kharasch and O. Reinmuth, *Grignard reactions of non-metallic substances*, Prentice-Hall, Englewood Cliffs, N.J., 1954, p. 1255.
13 A. Chakravorty and R. H. Holm, *Inorg. Chem.*, 3 (1964) 1521.
14 K. Noack, U. Schaerer and F. Calderazzo, *J. Organometal. Chem.*, 8 (1967) 517.
15 G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, 88 (1966) 3738.
16 J. A. Hill, J. M. Pratt and R. J. P. Williams, *J. Chem. Soc.*, (1964) 5149.
17 E. L. Muetterties and W. D. Phillips, in H. J. Emeléus and A. G. Sharpe (Eds.), *Advances in Inorganic Chemistry and Radiochemistry*, Academic Press, New York, 1962, Vol. 4, p. 231.
18 M. Gerloch, J. Lewis, F. E. Mabbs and A. Richards, *Nature*, 212 (1966) 809.
19 D. Hall and T. N. Waters, *J. Chem. Soc.*, (1960) 2644.