Substitution of Bi- and Mono-dentate Lewis Bases in Organocobalt(III) Complexes Holding a Tridentate Ligand: Routes to Novel Series of Organocobalt Compounds

I. YA. LEVITIN*, A. N. KITAIGORODSKII, A. T. NIKITAEV, V. I. BAKHMUTOV, A. L. SIGAN and M. E. VOL'PIN

Institute of Organo-Element Compounds, Academy of Sciences of the U.S.S.R., Moscow B-334, U.S.S.R.

Received November 19, 1984

Abstract

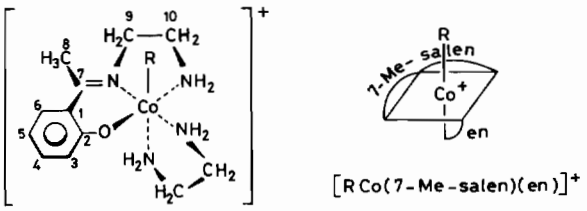
Routes have been designed to prepare new series of hexacoordinate cobalt(III) complexes containing a σ-bonded alkyl group (R), a mixed tridentate ligand and various mono- or bidentate Lewis bases. They consist of one or several reactions of either direct or proton-assisted ligand substitution, as exemplified by a model scheme for introducing two identical neutral monodentate ligands into the complexes with the planar tridentate anion o-$^{-}OC_6H_4C(Me)=N(CH_2)_2NH_2$ (7-Me-salen)$^{-}$:

$$[RCo(7\text{-Me-salen})(en)]^{+} \xrightarrow{LH^{+}} [RCo(7\text{-Me-salen})L_2]^{+} \xrightarrow{L'} [RCo(7\text{-Me-salen})L_2']^{+} \xrightarrow{L''H^{+}} [RCo(7\text{-Me-salen})L_2'']^{+}$$

Step 1 allows the chelating diamine in starting cation complexes to be replaced by weaker bases. Step 2 is suitable for introducing ligands effectively binding Co(III) ion, *viz.* typical chelating molecules and anions, or strong uniacidic bases. Step 3 permits the latter monodentate ligands to be exchanged for weaker bases. A variety of cationic, neutral and anionic complexes were thus obtained. Stoichiometry, stability and coordination geometry of these complexes are related to characteristics of newly introduced ligands (basicity, charge, steric requirements, ability to chelate). Their coordination in the *trans-R*-position was proved much looser and apparently less selective than that in the other (*cis*) one. ^{1}H and ^{13}C NMR spectra of complexes under consideration were studied in the course of this work.

Introduction

Only one type of organocobalt(III) complexes with a tridentate ligand has been reported so far. It is represented by cations of alkyl-*mer*-[N-(2-aminoethyl)-7-methylsalicylideneiminato](ethylenediamine)cobalt(+1) (**I**) and their close analogs [1, 2].



I

All are prepared via a template synthesis, and all contain a σ-bonded alkyl group, a chelating diamine and a tridentate ligand derived from a Schiff base composed of the same diamine and a ketoenol in 1:1 ratio. In neutral and alkaline media, these complexes are too inert to undergo direct ligand substitution [1], as well as alkylation of coordinated amino groups under the action of CH_3I. On the other hand, it is known that the complexes in question totally decompose in strongly acidic solutions [1, 3]. Since then we have found that certain intermediate conditions allow the chelating diamine to be exchanged for weaker bases, whether uni- or diacidic, via a proton-assisted process**. Monodentate ligands introduced in this way could be substituted directly, without protons being involved. Both the reactions were used to obtain a variety of organocobalt(III) complexes which have not yet been available. Results of these studies are presented below.

I. Studies of the Reactions in Solution

A. NMR Spectra of Starting Complexes of the [RCo(7-Me-salen)(en)]$^{+}$ Series

The evidence for the nature of the reactions under consideration is based mainly on ^{1}H and ^{13}C NMR

*Author to whom correspondence should be addressed.

**This finding has been briefly reported [4].

0020-1693/85/$3.30

TABLE I. Signals of Methyl and Aromatic Protons in ^{1}H NMR Spectra of Alkylcobalt(III) Complexes with the Tridentate Ligand *N*-(2-aminoethyl)-7-methylsalicylideneiminate(−1).[a]

A. Signals of methyl protons

Complex[b]	Solvent	Assigned signal: δ, ppm relative to TMS			
		R		7-Me-salen	Other ligands
		CH_3-Co	CH_3CH_2	CH_3-C	
[MeCo(7-Me-salen)(en)]$^+$	D_2O	2.22	–	2.50	
[MeCo(7-Me-salen)(H_2O)$_2$]$^+$		2.99	–	2.48	
[MeCo(7-Me-salen)(*c*-NH_3)(*t*-H_2O)]$^+$		2.29	–	2.58	
[MeCo(7-Me-salen)(*c*-py)(*t*-H_2O)]$^+$		2.46	–	2.64	
[EtCo(7-Me-salen)(en)]$^+$		–	0.54	2.50	
[EtCo(7-Me-salen)(*c*-CN)(*t*-H_2O)]		–	0.30	2.39	
[EtCo(7-Me-salen)(*c*-py)(*t*-H_2O)]$^+$		–	−0.10	2.64	
[EtCo(7-Me-salen)(py)$_2$]$^{+c}$		–	0.09	2.55	
[EtCo(7-Me-salen)(bpy)]$^+$		–	0.65	2.73	
[MeCo(7-Me-salen)(en)]$^+$	CD_3OD	2.12	–	2.50	
[MeCo(7-Me-salen)(MeOH)$_2$]$^+$		2.84	–	2.47	
[MeCo(7-Me-salen)(quil)][d]		3.24, 2.37	–	2.56, 2.62	
[EtCo(7-Me-salen)(en)]$^+$		–	0.56	2.47	
[EtCo(7-Me-salen)(MeOH)$_2$]$^+$		–	0.11	2.45	
[EtCo(7-Me-salen)(*c*-$MeNH_2$)(*t*-MeOH)]$^+$		–	0.13	2.51	(*c*-)CH_3NH_2: 2.01
[EtCo(7-Me-salen)(*c*-py)(*t*-MeOH)]$^+$		–	−0.12	2.62	
[EtCo(7-Me-salen)(*c*-OMe)(*t*-MeOH)]		–	0.09	1.89	
[EtCo(7-Me-salen)(quil)][d]		–	0.55, 0.69	2.62, 2.54	
[EtCo(7-Me-salen)(dppe)]$^+$	$CDCl_3$	–	0.29[e]	2.26	

B. Signals of aromatic protons

Complex[b]	Solvent	Assigned signal: δ, ppm relative to TMS				
		7-Me-salen (*o*-C_6H_4)				Other ligands
		(3)	(4)	(5)	(6)	
[MeCo(7-Me-salen)(en)]$^+$	D_2O	6.69	7.14	6.64	7.62	
[MeCo(7-Me-salen)(H_2O)$_2$]$^+$		6.94	7.24	6.72	7.66	
[MeCo(7-Me-salen)(*c*-NH_3)(*t*-H_2O)]$^+$		6.84	7.23	6.73	7.70	
[MeCo(7-Me-salen)(*c*-py)(*t*-H_2O)]$^+$		6.95	7.28	6.78	7.75	(*c*-)py: α, 8.55; β, 7.55; γ, 8.00
[EtCo(7-Me-salen)(en)]$^+$		6.74	7.14	6.66	7.64	
[EtCo(7-Me-salen)(*c*-py)(*t*-H_2O)]$^+$		6.96	7.26	6.76	7.76	(*c*-)py: α, 8.55; β, 7.55; γ, 8.00
[EtCo(7-Me-salen)(py)$_2$]$^{+c}$		6.93	7.30	6.78	7.68	
[EtCo(7-Me-salen)(bpy)]$^+$		6.28	6.95	6.57	≈7.70	bpy[f]: (3) 8.47, 8.57; (4) 8.17, 8.21; (5) ≈7.63, ≈7.73; (6) 8.91, 9.04
[MeCo(7-Me-salen)(en)]$^+$	CD_3OD	6.64	6.98	6.45	7.47	
[MeCo(7-Me-salen)(MeOH)$_2$]$^+$		6.92	7.08	6.53	7.51	
[MeCo(7-Me-salen)(quil)][d]						quil: (2) 8.89, (3) 7.60, (4) 8.34, 8.70 [g] [g]

(continued on facing page)

TABLE I. *(continued)*

Complex[b]	Solvent	Assigned signal: δ, ppm relative to TMS					
		7-Me-salen (o-C_6H_4)				Other ligands	
		(3)	(4)	(5)	(6)		
[EtCo(7-Me-salen)(en)]$^+$		6.65	6.97	6.43	7.48		
[EtCo(7-Me-salen)(quil)][d]						quil: (2) 8.66, 8.83	(4) 8.15, 8.25

[a]Multiplicities and intensities of the signals are consistent with their assignments. [b]The symbols *c* and *t* in the formulae denote *cis* and *trans* positions of the ligands with respect to the Co–C bond; quil = quinolinolate-8. [c]Calculated spectrum (extrapolation to [py] = ∞). [d]A mixture of geometric isomers differing in the orientation of the bidentate ligand in the coordination sphere. Data for the prevailing form are presented first. [e]A multiplet with J(HP) ≈ 9 Hz and J(HH) ≈ 7.5 Hz. [f]Positions that are equivalent in the free ligand are denoted by the same numbers. [g]Not identified.

data; relevant assignments are summarized in Tables I and II.

The ^{1}H NMR spectra of the starting complexes [RCo(7-Me-salen)(en)]$^+$ (R = Me, Et) exhibit signals of the methyl groups. To assign the corresponding two singlets from the methylcobalt complex, the spectrum was compared with that of the complex deuterated at the methyl ligand (R = CD_3). In the case of the ethylcobalt complex, experiments with double resonance were used to identify the signals of diastereotopic protons of the CH_2 group bound to cobalt. They were shown to form an AB-system, with the peaks located between 3.3 and 3.5 ppm (in D_2O). Further, the system of o-phenylene protons is completely resolved in the spectra of both the complexes at 200 MHz. To attribute these signals, their multiplicities, as well as qualitative electronic effects of the substituents in the benzene ring, were taken into account. The resulting assignments are consistent with those for o-disubstituted benzenes [5] and, in particular, for salicylaldiminates of Co(III) and Ni(II) [6].

The experimental $^{13}C\{^1H\}$ NMR spectrum of [MeCo(7-Me-salen)(en)]$^+$ was incomplete, lacking the resonances of the knot carbon atoms (C1, C2 and C7), evidently because of poor solubility of its (nitrate) salt*. A single high-field peak can be readily assigned to the methyl ligand. Just like the related signals in the spectra of other methylcobalt(III) complexes [7], it is broadened due to the interaction with the quadrupole ^{59}Co nucleus. Further analogies, namely those with the known ^{13}C NMR spectra of some related Schiff base complexes [7–9], allowed most of the other signals observed to be attributed to carbons of the tridentate ligand. The remaining close couple of lines at *ca.* 43 ppm should be assigned to carbon atoms of the en ligand.

B. Substitution of the Chelating Diamine by Donor Solvent under the Action of a Strong Acid

Step-by-step addition of small portions of perchloric acid to an aqueous or methanolic solution of [MeCo(7-Me-salen)(en)]$^+$ results in gradual replacement of the original ^{1}H NMR spectrum by a new one. Intensities of both spectra change linearly with $HClO_4$ added, and this process comes to completion when a 2:1 acid to complex ratio is reached**. Subsequent addition of alkali (NaOH) restores the original spectrum.

Similar results were obtained in the case of [EtCo(7-Me-salen)(en)]$^+$, with the only difference that the latter complex decomposes (see footnote) because of its higher sensitivity towards acids [3].

The above behaviour of [RCo(7-Me-salen)(en)]$^+$ complexes under the action of acid evidently corresponds to a reversible reaction being slow in the NMR time scale, with a large equilibrium constant, and involving two protons. The reversibility of the process under consideration suggests a product retaining the Co–C bond. Hence, one of new singlets in the ^{1}H NMR spectrum of the methylcobalt complex must be attributed to methyl ligand in this organometal species. An experiment with [CD_3Co(7-Me-salen)(en)]$^+$ allowed the signal in question to be identified.

The new signals also include resonances of enH_2^{2+} ion[†]: δ(^{1}H) = 3.38 ppm (s) (in D_2O[††]), δ(^{13}C) = 38.26 ppm (in CH_3OH) (the assignments are based on

*In the case of a more soluble product of the substitution of en, [MeCo(7-Me-salen)(py)H_2O]NO_3, all the expected signals were detected.

**Slow changes of intensities of the signals were noticed at high conversions. They can be explained by progressive total degradation of the complex under the action of acid [1, 3].

†,††For footnotes see overleaf.

TABLE II. ^{13}C NMR Signals of Methylcobalt(III) Complexes with the Tridentate Ligand *N*-(2-aminoethyl)-7-methylsalicylideneiminate(−1).

Complex	Solvent	Assigned signal: δ, ppm relative to TMS										
		CH_3–Co	7-Me-salen[a]								Other ligands	
			(1)	(2)	(3)	(4)[b]	(5)	(6)[b]	(7)	(8)	(9)	(10)	
[MeCo(7-Me-salen)(en)]$^+$	CH_3OH	0.0(br)	c	c	115.2	132.8	124.4	131.1	c	18.9	57.2	46.2	en: 42.9, 43.0
[MeCo(7-Me-salen)(*c*-py)(*t*-H_2O)]$^+$	D_2O	2.7(br)	125.3	164.9	117.6	134.4	124.8	132.6	173.6	20.8	58.2	43.1	(*c*-)py: α, 154.5; β, 126.9; γ, 140.5
[MeCo(7-Me-salen)($MeOH_2$)]$^+$	CH_3OH	c	c	c	115.9	133.1	124.0	131.0	c	19.0	58.1	42.5	

[a]The numbering of carbon atoms in this ligand is given in Formula I. [b]The tentative assignment of this close couple of lines is suggested by analogy with that of corresponding signals from the 'parent' aromatic molecule *o*-HOC_6H_4COMe as well as from *o*-HOC_6H_4CHO [10]. Yet it should be noted that in the case of related Schiff base complexes the alternative assignment, with $\delta_4 < \delta_6$, was given without discussion [7, 9]. [c]Not identified.

the comparison with the signals of the corresponding solutions of en·2HCl). Comparing intensities of the ^1H NMR signal of enH_2^{2+} with those of methyl ligands in the starting complex and in the product leads to conclusion that one enH_2^{2+} ion and one species of the organocobalt product are formed per ion of the starting complex consumed. This stoichiometry suggests that enH_2^{2+} may be generated due to either protonation–de-coordination of the chelating diamine, or acidolysis of the tridentate ligand. The latter alternative is hardly consistent with the ^{13}C NMR data: there are two new lines, apart from the signal of enH_2^{2+}, in the spectral region 40–60 ppm characteristic of $\underline{C}H_2$ resonances*. A wide separation (*ca.* 15 ppm) of these lines suggests that two linked methylene groups remain essentially non-equivalent, thus indicating the preservation of the Schiff base framework. The assumption that both en and the Schiff base may have been released would contradict experimental results (three rather than two protons should have been consumed), as well as literature evidence [11] for the instability of such Schiff bases with respect to disproportionation in protolytic media. Thus the resulting cobalt complex must hold the tridentate ligand as well as the Co–C bond. Hence the process under consideration can be presented by the following equation:

$$[MeCo(7\text{-Me-salen})(en)]^+ + 2H^+ \rightleftharpoons MeCo(7\text{-Me-salen})^+ + enH_2^{2+} \quad (1)$$

On this ground, the remaining lines in the newly arisen NMR spectra were attributed to the tridentate ligands in the organometallic products and assigned as in the case of the starting complexes [RCo(7-Me-salen)(en)]$^+$.

As for coordination state of the resulting complexes, a donor solvent (solv) like H_2O or MeOH is certainly able to enter one of the two coordination sites left by the diamine which lies in the plane of the tridentate ligand (*cis-R*-position). The above conclusion is based on the existence of rather stable complexes containing other monodentate Lewis bases

†Strictly, the equilibrium must involve both the acids conjugated with en, *i.e.* enH^+ as well as enH_2^{2+}. Accordingly, the ^1H NMR signal shifts somewhat downfield as the acid to complex ratio is raised, *i.e.* with decreasing pH. Nevertheless, an analysis of the NMR data revealed that enH_2^{2+} predominates over enH^+ under the conditions used. As for the values of chemical shifts given in the main text, they refer to solutions with acid to complex ratio *ca.* 2:1.

††The corresponding signal in CD_3OD must be hidden under a residual absorption of the solvent.

*As for the experimental ^1H NMR spectra, the $C\underline{H}_2$ resonances of both the chelating ligands (7-Me-salen and en) are obscure. Probably, they are concealed due to the involvement of the protons in complicated systems.

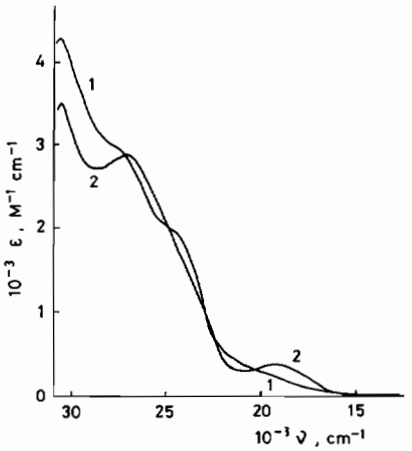


Fig. 1. Electronic spectra of $[MeCo(7\text{-Me-salen})(en)]^+$ (curve 1–1) and of the product of the decoordination of ethylenediamine (curve 2–2); aqueous solutions, 25 °C.

in this position (see below, Sect. I, D and II). It is less clear whether the sixth coordinatin site (*trans-R*-position) is occupied by another solvent molecule or not. The former alternative is suggested by direct analogy with related hexacoordinate complexes, including monodentate Lewis bases other than H_2O and MeOH (see below, Sect. I, D and II). Even the complexes with strongly donating monodentate anion ligands were isolated in the form of hydrates, *i.e.* apparently as hexa- rather than pentacoordinate compounds $[RCo(7\text{-Me-salen})A(H_2O)]$. On the other hand, the electronic spectrum of the product in question includes a long-wave band (Fig. 1) which resembles those characteristic of pentacoordinate organocobalt(III) complexes with tetradentate Schiff bases [12, 13], and hence may indicate some presence of the pentacoordinate form, $[RCo(7\text{-Me-salen})(cis\text{-}R\text{-solv})]^+$.

C. Substitution of the Chelating Diamine by Weaker Bases under the Action of the Conjugate Acids

The ^1H NMR technique was used to follow ligand substitutions in more complicated quaternary systems $[RCo(7\text{-Me-salen})(en)]^+$–$H^+$–L–solv, where R = Me or Et, solv = MeOH or H_2O, and L denotes typical Lewis base. In all cases conjugate acids LH^+ (*i.e.* L·HX salts) rather than a free strong acid were employed as sources of protons, which allowed the acid-induced degradation of complexes (Sect. II, A) to be substantially reduced.

No reaction was observed in the case of bases which are stronger than en, *viz.* those with $pK_a(L) > pK_{a2}(en) = 7.0$ (NH_3, $MeNH_2$, piperidine, CN^-, OH^-). On the other hand, new signals appear in the systems involving weaker bases (py, 4-Me-py, $PhNH_2$, NH_2OH, PPh_3). The resulting spectra are almost independent of time (*cf.* footnote **, p. 67), and the initial pattern is restored on adding alkali. These facts are again (*cf.* Sect. I, B) indicative of reversible processes which are fast with respect to time of measurements (minutes), but slow in the NMR time scale (seconds). Further, while in the case of PPh_3 (R = Et, solv = MeOH) the only 'new' component of the spectrum was due to the product of substituting en by the solvent, $[EtCo(7\text{-Me-salen})(MeOH)_2]^+$, the other systems gave extra sets of lines. Analysis of the new signals (particularly in the well-resolved high-field region of the spectra) suggests one more kind of organocobalt complexes to be formed in each of the systems. The nature of these species as the products of substitution of en by the Lewis bases was directly proved for the systems with L = py and R = Et. Namely, in this case the bispyridinate complex $[EtCo(7\text{-Me-salen})(py)_2]^+$ was isolated (in the form of bromide salt, see Sect. II, A), and its ^1H NMR spectra both in aqueous and methanolic solutions were found to be identical with the new sets of lines arising in the corresponding systems.

The spectra of the complex exhibit the non-equivalence of the two py molecules. One of them is evidently bound more loosely than the other: in water its signal is identical with that of the free base, thus indicating the complete dissociation of the complex. The observed non-equivalence of py ligands reveals that the substitution of the chelating diamine does not affect the mutual position of the remaining ligands R and 7-Me-salen [22] so that complexes in question have structure **II** rather than **III**.

II **III**

Since a strong labilizing *trans*-effect of an alkyl ligand is characteristic of organocobalt(III) chemistry [14, 15] including $[RCo(7\text{-Me-salen})(en)]^+$ [1], it can be concluded that in complexes of the type $[RCo(7\text{-Me-salen})L_2]^+$ the weaker bound Lewis base is in the *trans-R*- rather than the *cis-R*-position*.

D. Substitution of Monodentate Lewis Bases

The ^1H NMR technique was then used to study ligand exchange in the systems $[RCo(7\text{-Me-salen})(py)_2]^+$–py–water ($D_2O$ as a solvent) and $[RCo(7\text{-Me-salen})(py)_2]^+$–$MeNH_2$ (in $CDCl_3$). The spectra obtain-

*The labilization of this ligand may be also favoured by the presence of a planar polydentate ligand (in our case 7-Me-salen) with a system of conjugated bonds and a high donor strength. Such a *cis*-effect can be noticed in cobalt(III) complexes with tetradentate equatorial ligands [14, 15].

ed in the former case for both the complexes, with R = Me and Et, contained two sets of lines due to py*, but only one due to the R and 7-Me-salen ligands. Chemical shifts of the signals depend on py concentration in such a way that suggests a fast (in the NMR time scale) and reversible decoordination of one py molecule. Then, on the ground of results discussed in Sect. I, B and C, it can be concluded that the process under consideration consists of ligand substitution at the *trans-R*-position:

$$[RCo(7\text{-Me-salen})(py)_2]^+ + H_2O \rightleftharpoons$$

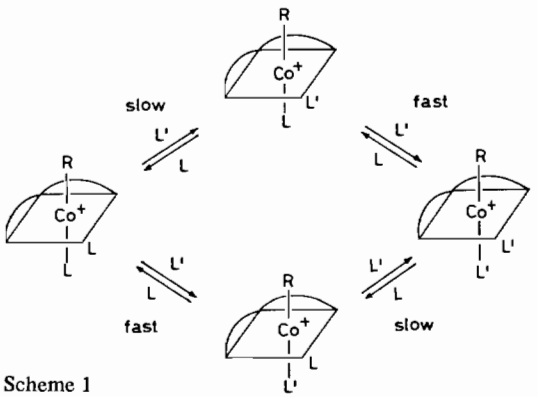
$$[RCo(7\text{-Me-salen})(c\text{-py})(t\text{-}H_2O)]^+ + py \qquad (2)$$

(For the sake of brevity, symbols *c* and *t* are used in formulae to denote the *cis*- and *trans-R*-position respectively)

A quantitative treatment of the experimental relationships between δ and [py] for the ethylcobalt complex allowed the equilibrium constant of reaction (2) (stability constant of $[EtCo(7\text{-Me-salen})(py)_2]^+$) to be calculated: $K = 1.9\ M^{-1}$ (25 °C, D_2O). Its comparison with the corresponding value for ethyl(pyridine)cobaloxime, $[EtCo(dmgH)_2(py)]$ ($K \approx 4 \times 10^3\ M^{-1}$ [16]) shows that the cationic RCo(7-Me-salen)(*c*-py)$^+$ residue is a harder acid than is the neutral $RCo(dmgH)_2$.

More complicated equilibria were observed in the systems $[RCo(7\text{-Me-salen})(py)_2]^+$–$MeNH_2$. The ^1H NMR spectra in $CDCl_3$ solutions evidently consist of coupled sets of lines from each of the ligands (R, 7-Me-salen, py and $MeNH_2$), both the intensities and chemical shifts of all the resonances depending on the complex to $MeNH_2$ ratio. Analysis of the experimental data shows that in the systems under consideration an exchange of the Lewis bases occurs at two non-equivalent sites, the ligand substitution at one of them being fast while at the other slow in the NMR time scale. Since the fast exchange, according to the above consideration, must take place at the *trans-R*-position, the equilibria in question are presented in Scheme 1**.

In aqueous or methanolic solutions similar ligand exchanges, which were examined for L = py and a short series of L′ ($MeNH_2$, NH_3, CN^-, OH^-), are naturally even more complicated because of the competition of the donor solvents for the sixth (*i.e. trans-R*) coordination site. The reaction pattern becomes simpler at low concentrations of L′ when these sites are virtually occupied by solvent molecules (*cf.* Sect. I, C). Under these conditions the



Scheme 1

^1H NMR signals can be referred to the individual complexes, $[RCo(7\text{-Me-salen})(c\text{-py})(t\text{-solv})]^+$ and $[RCo(7\text{-Me-salen})(c\text{-L}')(t\text{-solv})]^+$. Thus the comparison of their intensities allowed the following sequence for the ligand displacement at the *cis-R*-position to be established:

$$OH^-, OMe^- > MeNH_2 > NH_3 > py > CN^- \gg H_2O, MeOH$$

According to this reactivity series, the cationic residue $[RCo(7\text{-Me-salen})(t\text{-}R\text{-solv})]^+$ should be regarded as a hard acid.

II. Preparative Aspect of the Ligand Substitutions

A. Syntheses of Novel Organocobalt(III) Complexes

The reactions of ligand substitution considered above were used for preparing new series of cobalt complexes holding two of the original ligands, *viz.* a σ-bonded alkyl group and a tridentate Schiff base ligand. First, to replace the chelating diamines in the starting complexes, $[RCo(7\text{-Me-salen-}N\text{-}R^1)(N\text{-}R^1\text{-en})]^+$, with $R^1 = H^\dagger$ or Me, by weaker bases, both mono- (py) and bidentate ($o\text{-}C_6H_4(NH_2)_2$ = oph) ones, the corresponding conjugate acids were employed as reagents. Second, the direct exchange of monodentate Lewis bases in complexes obtained in this way permitted the introduction of ligands that effectively bind the metal ion. Namely, this route proved useful for preparing complexes with typical chelating ligands (bpy, quinolinolate-8 = $(quil)^-$, $o\text{-}C_6H_4O_2^{2-} = (cat)^{2-}$), as well as those with strong uniacidic bases (OH^-, SCN^-) in the *cis-R*-position (*cf.* Sect. I, D). Finally, substituting the hydroxide ligand in complexes of the latter type by a weaker base (NH_3) under the action of the conjugate acid (NH_4^+) was carried out to also prove helpful for synthesis.

Thus we prepared a range of cationic, neutral and anionic complexes of the following types: $[RCo(7\text{-Me-salen-}N\text{-}R^1)L_2]^+$ (L = py), [RCo(7-Me-salen-

*Strictly, two multiplets from β- as well as from γ-protons are observed whereas resonances of α-protons are evidently overlapping.

**The complete pattern may also involve pentacoordinate complexes (see Sect. I, B).

†7-Me-salen-*N*-R^1 = 7-Me-salen in this case.

TABLE III. Comparison of ^{1}H NMR Data for Methylcobalt(III) Complexes with Tridentate Schiff Base Ligands Derived from Ethylenediamine and *N*-Methylethylenediamine (7-Me-salen-*N*-R^1, with R^1 = H or Me).

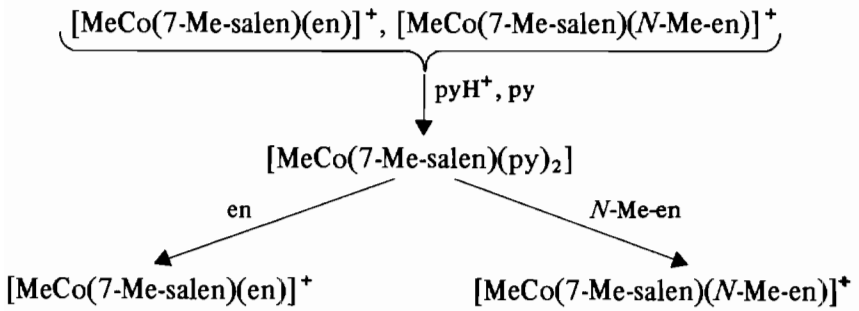
Substituents		Assigned signal[a]: δ (ppm relative to TMS), multiplicity							
R^1	R^2	CH_3-Co	*N*-R^2-en	7-Me-salen-*N*-R^1					
			CH_3-N	CH_3-N	CH_3-C	*o*-C_6H_4			
						(3)	(4)	(5)	(6)
(a) [MeCo(7-Me-salen-*N*-R^1)(*c*-NH_3)(*t*-H_2O)]$^+$ in D_2O									
H	–	2.29, s	–	–	2.58, s	6.84, dd	7.23, ddd	6.73, ddd	7.70, dd
Me[b]	–	2.33, s;	–	1.84s[c]	2.57, s;	6.82, d	7.21, dd	6.73, dd;	7.68, d;
		2.34, s		2.06, s[c]	2.58, s			6.70, dd	7.70, d
(b) [MeCo(7-Me-salen-*N*-R^1)(*N*-R^2-en)]$^+$ in CD_3OD									
H	H	2.12, s	–	–	2.50, s	6.64, dd	6.98, ddd	6.45, ddd	7.47, dd
H	Me	2.02, s	2.37, s[d]	–	2.54, s	6.67, dd	6.99, ddd	6.45, ddd	7.49, dd
Me	H	2.15, s	–	1.81, d[e]	2.51, s	6.63, dd	6.96, ddd	6.44, ddd	7.45, dd
Me	Me	2.08, s	2.32, s[d]	1.82, d[e]	2.55, s	6.68, dd	6.98, ddd	6.46, ddd	7.48, dd

[a]Intensities of the signals are consistent with their assignments. [b]Coupled signals of diastereomeric forms of this complex are listed in an arbitrary order, *viz.* that of increasing δ. [c]Doublet in H_2O, with $J \approx 6$ Hz. [d]Doublet in CD_3OH, with $J \approx 6$ Hz. [e]These splittings ($J \approx 5.5$ Hz) are due to hydrogen atom which is bonded to the nitrogen and does not undergo exchange for deuterium under conditions used. The assignment is based on experiments with double resonance.

N-R^1)(*c*-L)(*t*-H_2O)]$^+$ (L = NH_3), [RCo(7-Me-salen-*N*-R^1)(L–L)]$^+$ (L–L = oph, bpy or *N*-R^2-en, with R^2 = H or Me), [RCo(7-Me-salen-*N*-R^1)(*c*-A)(*t*-H_2O)] (A = OH or SCN), [RCo(7-Me-salen-*N*-R^1)(A–L)] (A–L = quil), [RCo(7-Me-salen-*N*-R^1)(A–A)]$^-$ (A–A = cat). A complex with one more chelating ligand, $Ph_2P(CH_2)_2PPh_2$ (dppe), was formed (from [EtCo(7-Me-salen)$(py)_2$]$^+$ and dppe) in solution, as evidenced by ^{1}H NMR and ion-exchange TLC data (Tables I, A and V), but could not be isolated under conditions used in similar cases, apparently because of the de-coordination of the diphosphine. The high lability of the dppe ligand is obviously indicative of steric hindrance to introducing bulky ligands. This conclusion is supported by molecular models revealing the *cis-R*-position to be particularly overcrowded.

To obtain the complexes with two identical neutral Lewis bases (py), a large excess of the free ligand was used. It is needed to suppress ligand substitutions involving donor solvents (see Sect. I, D). In the case of introducing monodentate anions (OH^-, SCN^-), even such conditions yielded, however, complexes including only one ligand in question. This fact is apparently due to a reduced positive charge on the metal by the strongly donating coordinated anion.

Two specific applications of the reactions studied are noteworthy. First, in the course of this work we found that the template syntheses of the methylcobalt complexes [MeCo(7-Me-salen)(en)]X (X = Br, I) [1, 2] were accompanied by the formation of the related complexes with the *N*-methylated diamine, [MeCo(7-Me-salen)(*N*-Me-en)]X. Separation of the couple products by fractional crystallization (from H_2O, MeOH or Me_2CO) or ion-exchange chromatography meets with difficulties. On the other hand, these mixtures can be easily converted into either complex via the following route composed of the ligand substitutions (Scheme 2).



Scheme 2.

TABLE IV. Analytical Data for Alkylcobalt(III) Complexes with Tridentate Schiff Bases.

Complex	Found (calculated), %					
	C	H	N	Co	Other elements	H_2O
[EtCo(7-Me-salen)(en)]Br	41.5 (41.5)	6.3 (6.5)	14.0 (13.8)	13.9 (14.5)	Br: 19.7 (19.7)	
[EtCo(7-Me-salen)(py)$_2$]Br	52.5 (52.5)	5.6 (5.6)	11.3 (11.1)	11.6 (11.7)	Br: 14.4 (15.9)	
[MeCo(7-Me-salen)(NH_3)(H_2O)]I			10.4 (10.2)			
[MeCo(7-Me-salen-*N*-Me)(NH_3)(H_2O)]I			10.2 (9.8)			4.7 (4.2)
[EtCo(7-Me-salen)(oph)]Br	48.2 (47.8)	5.6 (5.8)	12.2 (12.4)	13.3 (13.0)	Br: 17.6 (17.6)	
[MeCo(7-Me-salen)(OH)(H_2O)]	47.5 (46.6)	6.1 (5.7)	9.8 (9.9)	19.9 (20.8)		12.9 (12.7)[a]
[MeCo(7-Me-salen)(SCN)(H_2O)]	46.2 (44.0)	4.9 (5.5)		17.9 (18.0)	S: 9.4 (9.8)	5.5 (5.5)
Na[MeCo(7-Me-salen)(cat)]					Na: 5.7 (6.0)	

[a]Corrected to allow for the titration of hydroxide ion by Fischer reagent [23].

According to ^{1}H NMR data, the substitution of the py ligands by *N*-Me-en results in the formation of the same geometric isomer which is present in the original mixture (see Sect. II, B).

Second, syntheses via the hydroxo complexes provide an opportunity to prepare cation complexes with a desired counter-ion (Scheme 3).

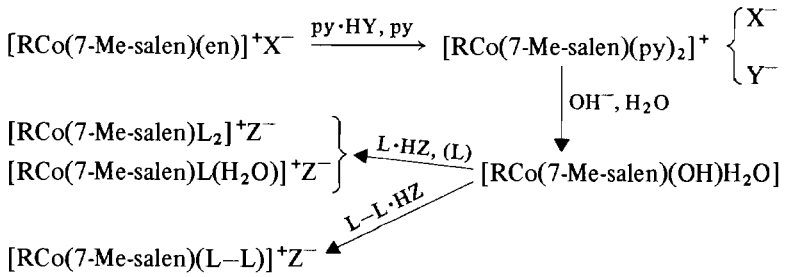
In this respect, the above procedure can be regarded as a helpful alternative to ion metathesis in solution or the use of ion-exchange chromtography.

B. Identification of the Complexes and Elucidation of Their Structures

All the complexes prepared decompose readily in strongly acidic solutions, just as the [RCo(7-Me-salen)(en)]X salts do [1]. To establish the formulae of the complexes under study, we made use of identifying products of their decomposition in acidic medium ('acidolysis'), as well as ^{1}H NMR spectral data (Tables I and III), and results of elemental and aquametric analyses (Table IV).

Certain further structural information came from IR spectra. In particular, all show absorption in the range 1440–1620 cm^{-1}, consisting of 3–4* intense bands evidently due to in-plane vibrations of the conjugated system of the tridentate ligand. The strong band arising between 710 and 770 cm^{-1} can be assigned to out-of-plane deformation mode of C–H bonds in the *o*-disubstitued benzene ring of the same ligand. Further, all the spectra exhibit C–H stretches characteristic of CH_3, CH_2 and C(arom)–H groups, as well as a rather strong absorption (in the region 3120–3350 cm^{-1}) due to stretching vibrations of N–H bonds in coordinated amino groups. In many cases, the frequencies at which ν(N–H) bands appear, as well as their widths and intensities, indicate the existence of intermolecular (or inter-ion) H-bonding. In particular, this is

*Unless the complex includes other ligands (*e.g.* aromatic or heterocyclic) absorbing in the same region.



Scheme 3.

TABLE V. Characterization of Alkylcobalt(III) Complexes with Tridentate Schiff Bases by TLC on SiO_2 ('Silufol' plates).

Complex	Eluent	R_f
$[MeCo(7\text{-Me-salen})L_2]^+$ $[MeCo(7\text{-Me-salen})L(solv)]^+$	0.1 M NaOAc in MeOH–H_2O 4:1 (v/v)	0.52[a]
$[MeCo(7\text{-Me-salen})(en)]^+$		0.29
$[MeCo(7\text{-Me-salen})(N\text{-Me-en})]^+$		0.32
$[MeCo(7\text{-Me-salen-N-Me})L_2]^+$ $[MeCo(7\text{-Me-salen-N-Me})L(solv)]^+$		0.55[a]
$[MeCo(7\text{-Me-salen-N-Me})(en)]^+$		0.29
$[MeCo(7\text{-Me-salen-N-Me})(N\text{-Me-en})]^+$		0.34
$[EtCo(7\text{-Me-salen})L_2]^+$ $[EtCo(7\text{-Me-salen})L(solv)]^+$		0.51[a]
$[EtCo(7\text{-Me-salen})(en)]^+$		0.32
$[EtCo(7\text{-Me-salen})(oph)]^+$		0.52
$[EtCo(7\text{-Me-salen})(bpy)]^+$		0.23
$[EtCo(7\text{-Me-salen})(dppe)]^+$		0.65
$[MeCo(7\text{-Me-salen})(quil)]$[b]	MeOH–py 19:1 (v/v)	0.53
$[EtCo(7\text{-Me-salen})(quil)]$[b]		0.53

[a]This value is virtually independent of the nature of monodentate Lewis bases (L and solv). [b]A mixture of isomers.

true for cation complexes with halide and nitrate, but not perchlorate counter-ions. The appropriate spectra also provided evidence for the presence of certain specific ligands or counter-ions. Thus the thiocyanate complex, $[MeCo(7\text{-Me-salen})(SCN)H_2O]$, was characterized by the $\nu(CN)$ band at 2100 cm^{-1} (vs). Further cation complexes with perchlorate and nitrate counter-ions exhibit well-known bands of these anions, in particular ν_3 at *ca.* 1100 and 1400 cm^{-1} (both vs) for ClO_4^- and NO_3^- respectively. As to the spectra of complexes with suggested water or hydroxide ligands, they do contain broad bands of medium intensity in the region typical of O–H stretches (3200–3600 cm^{-1}). However, these absorptions can hardly be relied on to establish the presence of the ligands in question because of possible intervention of crystallization water and overlapping N–H bands.

The complexes with a bidentate ligand proved stable enough to be characterized by TLC (Table V); namely, ion exchange and adsorption variants of the chromatographic technique were used in the cases of cationic and neutral complexes respectively. On the other hand, complexes with various monodentate Lewis bases were found indistinguishable by TLC under similar conditions (the same Table), which agrees well with the NMR evidence for the lability of these ligands (Sect. I, D). It is apparent that under conditions of ion-exchange TLC the Lewis bases are displaced by some component(s) of an eluating electrolyte.

The relative stability of the complexes with typical bidentate ligands suggests that the latter chelate the metal ion as en does in the starting compounds. Then, because of steric requirements of both the polydentate ligands present, the complexes in question should, irrespectively of the course of ligand substitution, retain the initial coordination geometry (**I**), with the Schiff base ligand holding meridional position and the bidentate ligand occupying adjacent (*cis-* and *trans-R*) coordination sites. This essentially asymmetric structure is quite consistent with NMR data, revealing distinct non-equivalence of all protons in the coordinated bpy (Table I, B). As shown in Sect. II, A, the related geometry (**II**) is characteristic of the complexes with monodentate Lewis bases. Hence, the introduction of two dissimilar monodentate ligands or a chelating one lacking mirror symmetry may yield two geometric isomers. This conclusion was proved basically true in the former case (see Sect. I, D) although related equilibria (3) are favourable to the fomation of complexes with the stronger bases in the *cis-R*-position. A further confirmation came from a review of the ^1H spectra (Table I) showing the quinolinolate-8 complexes to be a mixture of two isomers. On the other hand, NMR as well as TLC data (Tables III and V) suggest that the substitution of two py ligands by *N*-Me-en results in the formation of a single complex which is identical with that prepared by the template synthesis (see Sect. II, A). To elucidate its structure, a comparison of ^1H NMR spectra of some related methylcobalt complexes (Table III) may be useful. In particular, the resonance of methyl ligand in the complex under consideration is markedly shifted upfield (by 0.10

ppm) against the corresponding signal from [MeCo(7-Me-salen)(en)]$^+$ while methylation of the latter complex at one of *cis-R*-amino groups, *viz.* that in the tridentate ligand, results in a smaller and opposite effect (0.03 ppm downfield). Thus, it can be assumed that the bidentate ligand in the [MeCo(7-Me-salen)(*N*-Me-en)]$^+$ complex obtained is coordinated in such a way that the methylamino group is in the *trans-R*-position.

Finally, the ^{1}H NMR spectrum of [MeCo(7-Me-salen-*N*-Me)(*c*-NH_3)(*t*-H_2O)]$^+$ (Table III) reveals the presence of nearly equal amounts of two diastereomeric forms differing in the position of the substituents in amino group (H and Me) with respect to the plane of the tridentate ligand. By contrast, the spectra of related diamine complexes, [MeCo(7-Me-salen-*N*-Me)(en)]$^+$ and [MeCo(7-Me-salen-*N*-Me)(*N*-Me-en)]$^{+*}$ (the same Table), are characteristic of individual species. The absence of another diastereomer here can be explained by steric hindrance to the formation of the complexes with the methyl substituent (in the amino group of the tridentate ligand) directed towards the chelating diamine.

III. Experimental

A. Precautions

Needed because of photo- and thermo-lability of organocobalt(III) complexes with tridentate Schiff bases. The complexes were generally protected from light. During evaporation of their solutions (under vacuum), the bath temperature was kept below 40 °C.

B. Materials

The starting complexes with the tridentate Schiff base derived from *o*-HOC_6H_4COMe and en, *viz.* the individual [EtCo(7-Me-salen)(en)]X salts and the mixtures of [MeCo(7-Me-salen)(en)]X and [MeCo(7-Me-salen)(*N*-Me-en)]X (X = Br or I), were prepared via the known template procedures [2]; to obtain a mixture of the deuterated methylcobalt complexes, [CD_3Co(7-Me-salen)(en)]I and [CD_3Co(7-Me-salen)-(*N*-CD_3-en)]I, CD_3I was used as alkylating agent instead of CH_3I. The starting methylcobalt complex with the Schiff base derived from *o*-HOC_6H_4COMe and *N*-Me-en, [MeCo(7-Me-salen)-*N*-Me)(*N*-Me-en)]I, was synthesized in a similar way using *N*-Me-en in lieu of en; the yield was 36%. The corresponding nitrate salts (X = NO_3) of both the series were prepared as follows. To methanol solutions of the iodides (X = I), a concentrated aqueous solution of Pb-(NO_3)$_2$ was added dropwise until precipitation of PbI_2 came to completion. The PbI_2 was filtered off, and the filtrates were diluted with water and then concentrated under vacuum. The products were allowed to crystallize at 0 °C, then separated by filtration, washed with a small amount of ice-cold water, and air-dried. They were identified by ion-exchange TLC and IR spectroscopy; *int. al.*, the former test proved virtual absence of Pb(II) and I^-.

N-Me-en was prepared by the known route to *N*-substituted ethylenediamines starting from HO-$(CH_2)_2NH_2$ [17–19] and characterized by b.p. 114–116 °C/745 Torr (lit. [20] 115–117 °C/757 Torr). Py·HNO_3 was obtained from py (5% excess) and nitric acid in aqueous medium; the resulting solution was evaporated to dryness under vacuum, and the salt was crystallized from EtOH. Commercial pyrocatechol was liberated from accumulated products of the autoxidation by vacuum sublimation. Other reagent grade chemicals were used without purification.

To obtain a reference solution of bis(quinolinolate-8)cobalt(II) for TLC, $Co(OAc)_2$ was allowed to react with quinolinol-8 in a neutral acetate buffer medium [21], which was followed by extraction of the product with CH_2Cl_2. A solution of (salH)en-*N*-Me for a similar use was prepared by interaction of *o*-HOC_6H_4CHO and *N*-Me-en in MeOH.

C. Spectral Studies

In all NMR experiments, concentrations of complexes were below 0.06 M. Since chemical shifts of the cation complexes in D_2O and CD_3OD proved insensitive to the counter ion (Br^-, I^-, ClO_4^- or NO_3^-), the latter was chosen arbitrarily, NO_3^- being often preferred because of better solubility of the nitrates. A 1.75 M stock solution of $HClO_4$ in D_2O was used as the source of protons. ^{1}H NMR spectra were taken at room temperature on Bruker Fourier spectrometers SXP-4-100 and WP-200-SY with TMS (in $CDCl_3$ and CD_3OD) or DSS (in D_2O) as internal standard. $^{13}C\{^1H\}$ NMR spectra were obtained at ambient temperature on the WP-200 instrument at 50.31 MHz with TMS (in CH_3OH) or t-BuOH (in D_2O) as internal standard.

Visible spectra were taken on a Carl Zeiss double-beam spectrometer Specord UV–Vis. The starting complex [MeCo(7-Me-salen)(en)]ClO_4 was examined in 2–10 mM aqueous solutions, with a small amount of en added. To obtain the spectrum of the product of the decoordination of en, the spectrum of one of the above solutions (A) was subtracted (using a reference cell) from that of a solution (B) prepared by dissolving the starting complex and $HClO_4$ so that their initial concentrations were *ca.* 7 mM each. The concentration of the complex in A was equal to its equilibrium concentration in B, the latter value being

*Concerning the orientation of the bidentate ligand, *N*-Me-en, in the coordination sphere, the above discussion (of the case of [MeCo(7-Me-salen)(*N*-Me-en)]$^+$) holds true.

calculated using results of the potentiometric study of reaction (1) [22].

IR spectra were taken on a Carl Zeiss spectrometer UR-20, generally with solid state samples, *viz.* KBr pellets (in the wide range of 400–3800 cm^{-1}), or fluorolub (f), hexachlorobutadiene (h) and nujol (n) mulls (mainly in the regions of N–H (f, h) and O–H (n) stretches) respectively.

D. Analyses

Elemental analyses*, except those for Na (see Sect. III, E, (13)), were carried out by conventional techniques. Aquametric analyses* were performed by coulometric modification of the K. Fischer method. TLC tests were run on either 'Silufol' or 'Silufol UV-254' plates (Kavalier, Czechoslovakia).

'Acidolysis' of methyl- and ethylcobalt complexes with tridentate Schiff bases and identification of its products

The basic procedure is outlined below while certain specific operations and analyses are described after the syntheses of corresponding complexes in Sect. III, E.

A sample under examination was treated with 2 M HCl acid under anaerobic conditions in a closed vial until visual changes were over (in some cases heating to 40–50 °C was necessary). A gas (headspace) sample was passed through aqueous alkali and then analyzed for C1-C4 hydrocarbons (*viz.* CH_4 and C_2H_6, or C_2H_4, C_2H_6 and n-C_4H_{10}) by GC with a Porapak Q column and a flame-ionization detector. The emulsion resulting from the 'acidolysis' was washed with CH_2Cl_2. After separation of the layers, the CH_2Cl_2 extract (solution A) was analyzed for *o*-HOC_6H_4COMe by TLC on 'Silufol UV-254' plates with CH_2Cl_2 as eluent. The aqueous solution was evaporated to dryness under vacuum; the residue was dissolved in a small amount of water. The resulting solution (B) was strongly alkalified with KOH under cooling and then reduced with $NaBH_4$ at 70 °C, the heating was continued until effervescence came to completion. After the decantation of a solution (C) from Co powder, volatile components were recondensed under vacuum. *o*-HOC_6H_4-CHO was added to the condensate dropwise until the reagent began to separate. 10 minutes later the mixture was centrifuged. A precipitate was dissolved in $CHCl_3$. In appropriate cases, both (or either) of the solutions obtained were (was) analyzed for the Schiff base(s): $(salH)_2$en (the solution in $CHCl_3$) and (or) (salH)en-*N*-Me (the aqueous solution), by TLC on 'Silufol' with $CHCl_3$ – AcOEt 9:1 and AcOEt – MeOH – Et_3N 8:1:1 mixtures (v/v), respectively, as eluents.

*Obtained at the analytical branch of this Institute.

E. Syntheses

(1) [EtCo(7-Me-salen)(py)$_2$]Br

py·HNO_3 (312 mg, 2.2 mmol), [EtCo(7-Me-salen)(en)]Br (405 mg, 1 mmol) and NaBr (0.2 g) were successively dissolved in MeOH (10 ml), which resulted in precipitation of en·2HBr**. It was filtered off. After adding py (0.7 ml), water (8 ml) and more NaBr (0.3 g) to the filtrate, it was concentrated under vacuum to *ca.* 5 ml. The product was allowed to crystallize at 0 °C, then separated by filtration washed with a small amount of cold mixture H_2O – py (15:1), and air-dried. Yield 383 mg (76%); orange-red needles.

(2) [MeCo(7-Me-salen)(c-OH)(t-H$_2$O)]

A solution of [MeCo(7-Me-salen)$(py)_2$]Br† (490 mg, *ca.* 1 mmol) in MeOH (10 ml) was poured into a solution of NaOH (160 mg, *ca.* 3.5 mmol) in water (20 ml) under cooling and stirring. The product was allowed to crystallize at 0 °C. Then it was separated by filtration, washed with a dilute (*ca.* 3 mM) aqueous solution of NaOH, and dried over $CaCl_2$. Yield 250 mg (88%); brick-red powder; Na content *ca.* 0.1%.

(3) [MeCo(7-Me-salen-N-Me)(c-NH$_3$)(t-H$_2$O)]I

(a) py·HNO_3 (310 mg, 2.2 mmol) and [MeCo(7-Me-salen-*N*-Me)(*N*-Me-en)]I (466 mg, 1 mmol) were successively dissolved in MeOH; then py (0.7 ml) and water (10 ml) were added. The resulting solution was concentrated under vacuum to *ca.* 7 ml and cooled at 0 °C to give a dark-crimson crystalline powder which was separated by filtration, washed with a small amount of ice-cold water and air-dried. Yield 460 mg.

(b) A reaction mixture of the latter (pyridinate) complex and NaOH (200 mg, *ca.* 4.5 mmol) in MeOH (10 ml) was stirred for an hour and then poured into a solution of NaOH (0.1 g) in water (10 ml) under cooling and stirring. The resulting suspension was reduced in volume to *ca.* 10 ml by vacuum evaporation. A precipitate was separated by filtration, washed with a dilute (*ca.* 3 mM) aqueous solution of NaOH and air-dried to yield 240 mg of brick-red powder.

(c) To a suspension of the latter (hydroxo) complex in MeOH (10 ml), NH_4NO_3 (160 mg, 2 mmol) was added under stirring. The resulting solution was diluted with water (10 ml) and concentrated under vacuum to *ca.* 8 ml. Then concentrated

**It was identified in the form of $(salH)_2$en (*cf.* Sect. III, D).

†This complex was prepared similarly to (1) starting from a mixture of [MeCo(7-Me-salen)(en)]Br and [MeCo(7-Me-salen)(*N*-Me-en)]Br. It partially loses py on storage.

aqueous NH_3 (2 drops) and saturated water solution of KI (0.5 ml) were successively added. The product was allowed to crystallize at 0 °C. Then it was separated by filtration, washed with a small amount of a cold dilute (*ca.* 0.1 M) aqueous NH_3, and air-dried. Yield 265 mg (62%); red powder. To convert the product into the diaquocomplex, $[MeCo(7\text{-Me-salen-}N\text{-Me})(H_2O)_2]^+$, one equivalent of an acid is required [22].

(4) [MeCo(7-Me-salen)(c-NH_3)(t-H_2O)] I

was prepared similarly to (3,c) starting from $[MeCo(7\text{-Me-salen})(OH)H_2O]$. Yield 77%; red powder.

(5) [MeCo(7-Me-salen)(c-SCN)(t-H_2O)]

A suspension of $[MeCo(7\text{-Me-salen})(OH)H_2O]$ (283 mg, 1 mmol) in MeOH (10 ml) was saturated with CO_2 until all the complex was dissolved, then KSCN (0.3 g, *ca.* 3 mmol) was added. The resulting solution was poured into a solution of KSCN (0.1 g, *ca.* 1 mmol) in water (7 ml) under cooling and stirring. The liquor thus obtained was concentrated under vacuum to *ca.* 5 ml.. The product was allowed to crystallize at 0 °C, separated by filtration, washed with a small amount of ice-cold water, and air-dried. Yield 165 mg (50%); carmine-red crystalline powder; K content < 0.1%.

(6) [EtCo(7-Me-salen)(oph)] Br

$o\text{-}C_6H_4(NH_2)_2$ (65 mg, 0.6 mmol), concentrated HBr acid (1.1 mmol of HBr) and $[EtCo(7\text{-Me-salen})(py)_2]Br$ (203 mg, 0.5 mmol) were successively dissolved in MeOH (5 ml), which resulted in precipitation of some en·2HBr which was filtered off. The filtrate was diluted with water (5 ml) and concentrated under vacuum to *ca.* 3 ml. The product was allowed to crystallize at 0 °C, separated by filtration, washed with a small amount of ice-cold water, and air-dried. Yield 130 mg (58%); reddish-brown powder.

To identify $o\text{-}C_6H_4(NH_2)_2$ as a product of the 'acidolysis' of the complex, an aliquot of the solution C was Et_2O-washed. The diamine was detected in the ether extract by TLC on a 'Silufol' plate with EtOH – NH_3 aq. 49:1 mixture (v/v) as eluent, the spot being developed by exposing to light (autoxidation).

(7) [EtCo(7-Me-salen)(bpy)] Br

A solution of $[EtCo(7\text{-Me-salen})(py)_2]Br$ (126 mg, 0.25 mmol) and bpy (44 mg, 0.28 mmol) in CH_2Cl_2 (5 ml) was heated at reflux for 2 h. After cooling, C_6H_6 (10 ml) was added to precipitate the product. It was separated by filtration, C_6H_6-washed, and air-dried. Yield 82 mg (65%); light-red powder.

(8) [MeCo(7-Me-salen)(en)] ClO_4

To a solution of $[MeCo(7\text{-Me-salen})(py)_2]Br$* (490 mg, *ca.* 1 mmol) in MeOH (5 ml), en (130 μl of a 70% aqueous solution, 1.5 mmol) and a saturated aqueous solution of $NaClO_4$ (2 ml) were successively added. The product was allowed to crystallize at 0 °C, separated by filtration, washed with a small amount of ice-cold water, and air-dried. Yield 300 mg (73%); red crystalline powder.

(9) [MeCo(7-Me-salen)(N-Me-en)] ClO_4

was prepared similarly to (8) using *N*-Me-en (130 μl, 1.5 mmol) instead of en. Yield 265 mg (64%), orange-red powder.

(10) [MeCo(7-Me-salen-N-Me)(en)] I

The pyridinate complex (3,a) obtained from $[MeCo(7\text{-Me-salen-}N\text{-Me})(N\text{-Me-en})]I$ (117 mg, 0.25 mmol) was dissolved in MeOH (10 ml). Then en (45 μl of a 70% aqueous solution, *ca.* 0.5 mmol), water (5 ml) and a saturated aqueous solution of NaI (0.2 ml) were successively added. The resulting solution was concentrated under vacuum to *ca.* 3 ml. A precipitate formed on cooling was separated by filtration, washed with cold water, and air-dried Yield 81 mg (70%); light-red powder.

(11) [MeCo(7-Me-salen)(quil)] (mixture of isomers)

A suspension of $[MeCo(7\text{-Me-salen})(OH)H_2O]$ (283 mg, 1 mmol) in MeOH (10 ml) was saturated with CO_2 until all the complex was dissolved. Then quilH (160 mg, 1.1 mmol) was added. After removing CO_2 under vacuum, a concentrated aqueous NH_3 (few drops) was introduced. A precipitate formed thereby was separated by filtration, washed with a small amount of MeOH, and air-dried. Yield 300 mg (76%); light-brown plates.

While analyzing 'acidolysis' products, an aliquot of the solution B was buffered with $NaHCO_3$ and CH_2Cl_2-washed. $[Co(quil)_2]$ was identified in the CH_2Cl_2 extract by TLC on a 'Silufol' plate with EtOH–NH_3 aq. 9:1 mixture (v/v) as eluent.

(12) [EtCo(7-Me-salen)(quil)] (mixture of isomers)

To a solution of $[EtCo(7\text{-Me-salen})(py)_2]Br$ (203 mg, 0.5 mmol) and quilH (80 mg, 0.55 mmol) in MeOH (4 ml), concentrated aqueous NH_3 (few drops) was added. The product was allowed to crystallize at 0 °C, separated by filtration, washed with a small amount of cold MeOH, and air-dried. Yield 130 mg (64%); brick-red powder.

*See footnote † p. 75.

(13) Na[MeCo(7-Me-salen)(cat)]

This was prepared and stored under anaerobic conditions. To a suspension of [MeCo(7-Me-salen)-$(py)_2$]Br* (490 mg, *ca.* 1 mmol) in MeOH (6.5 ml) were added a solution of *o*-$C_6H_4(OH)_2$ (127 mg, 1.15 mmol) in MeOH (2.5 ml) and then, under cooling, a solution of NaOH (110 mg, *ca.* 2.5 mmol) in MeOH (1 ml). The reaction mixture was reduced in volume to a half by vacuum evaporation and then diluted with water (5 ml). The product was allowed to crystallize at 0 °C, separated by centrifugation, washed with water until the solvent remained colourless, and dried *in vacuo*. Yield 176 mg (46%); brick-red powder.

While analyzing 'acidolysis' products, *o*-C_6H_4-$(OH)_2$ was identified in the same TLC test as *o*-HOC_6-H_4COMe was. Namely, it was detected after an additional elution, this time with MeOH, the spot being developed by exposing to light (autoxidation). To assay the Na content in the complex, an aliquot of the solution B was adjusted to pH 7–8 by adding CaO. The resulting solution was analyzed for Na^+ potentiometrically, using a 'sodium' glass electrode.

Acknowledgements

We thank Drs. Yu. N. Belokon' and L. A. Leites for helpful discussions, and Mr. R. M. Bodnar for technical assistance.

References

1 I. Levitin, A. Sigan, E. Kazarina, G. Alexandrov, Yu. Struchkov and M. Vol'pin, *J. Chem. Soc., Chem. Commun.*, 441 (1981).
2 I. Ya. Levitin, R. M. Bodnar and M. E. Vol'pin, *Inorg. Synth., 23,* in press.
3 I. Ya. Levitin, A. L. Sigan, R. M. Bodnar, R. G. Gasanov and M. E. Vol'pin, *Inorg. Chim. Acta, 76,* L169 (1983).
4 I. Ya. Levitin, A. N. Kitaigorodskii, A. T. Nikitaev, V. I. Bakhmutov, R. M. Bodnar, N. V. Plekhanova and M. E. Vol'pin, *Izvest. Akad. Nauk SSSR, Ser. Khim.*, 952 (1984).
5 W. B. Smith, A. M. Ihrig and J. L. Roark, *J. Phys. Chem., 74,* 812 (1970), and refs. therein.
6 D. Cummings, B. M. Higson and E. D. McKenzie, *J. Chem. Soc., Dalton Trans.*, 1359 (1973).
7 W. M. Coleman and L. T. Taylor, *J. Inorg. Nucl. Chem., 43,* 3217 (1981), and refs. therein.
8 G. Cros and J.-P. Costes, *C.R. Acad. Sci., Ser. B:, 294,* 173 (1982).
9 J.-P. Costes, G. Cros, M.-H. Darbieu and J.-P. Laurent, *Inorg. Chim. Acta, 60,* 111 (1982).
10 E. Breitmaier, G. Haas and W. Voelter, 'Atlas of Carbon-^{13}C NMR Data, Vol. 2', Heydon, London, 1979.
11 G. Cross and J.-P. Costes, *C.R. Acad. Sci., Ser. B:, 294,* 173 (1982) and refs. therein.
12 G. Costa, G. Mestroni and L. Stefani, *J. Organomet. Chem., 7,* 493 (1967).
13 A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani and G. Tauzher, *Inorg. Chim. Acta Rev., 4,* 41 (1970).
14 J. M. Pratt and R. G. Thorp, *Adv. Inorg. Chem. Radiochem., 12,* 375 (1969).
15 G. Costa, *Pure Appl. Chem., 30,* 335 (1972).
16 A. Crumbliss and W. K. Wilmarth, *J. Am. Chem. Soc., 92,* 2593 (1970).
17 R. O'Gee and H. M. Woodburn, *J. Am. Chem. Soc., 73,* 1370 (1951).
18 O. Hromatka, O. Kraupp and C. Skopalik, *Monatsch. Chem., 84,* 349 (1953).
19 K. Ward, Jr., *J. Am. Chem. Soc., 57,* 914 (1935).
20 S. R. Aspinall, *J. Am. Chem. Soc., 63,* 853 (1941).
21 I. V. Pyatnitsky, 'Analytical Chemistry of Cobalt' (in Russian), Nauka, Moscow, 1965, p. 100.
22 A. D. Ryabov, I. Ya. Levitin, A. T. Nikitaev, A. N. Kitaigorodskii, V. I. Bakhmutov, I. Yu. Gromov, A. K. Yatsimirsky and M. E. Vol'pin, *J. Organomet. Chem.*, submitted for publication.
23 J. Mitchell, Jr. and D. M. Smith, 'Aquametry, Part III', Wiley, New York, 1980.

*See footnote † p. 75.