Reactions of Complex Compounds of Cobalt. Part VIII.[1] Synthesis, Protonation, and Oxidative Degradation of Salicylatocobalt(III) Complexes

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A new synthesis of bis(ethylenediamine)salicylatocobalt(III) ion has been developed and extended to analogous complexes with the ligands 3-methylsalicylic, 5-methylsalicylic, and 3-hydroxy-2-naphthoic acid. Salicylato- and 5-methylsalicylato-(triethylenetetramine)cobalt(III) salts have also been prepared. ^1H N.m.r. and electronic spectroscopy have been used to study protonation of several of these complexes and the results suggest that the site of attachment is the oxygen atom of the phenol group. All the complexes can be oxidatively degraded with acidic potassium permanganate to give corresponding oxalato-derivatives.

COMPLEXES of cobalt(III) containing the bidentate salicylate ion undergo reactions in which the organic moiety is modified whilst remaining bound to the metal ion. Rapid and reversible protonation in the presence of dilute mineral acids has long been known[2,3] but is not clearly understood. Intense green materials are obtained on treating the complexes $[Co(NH_3)_4(sal)]^+$ or $[Co(en)_2(sal)]^+$ [sal = salicylate(2-), en = ethylenediamine] with concentrated nitric acid.[2,3] The nature of these paramagnetic green products has been recently reinvestigated; whilst attack at the 5-position of the aromatic ring is unquestioned, the substances have been variously formulated as nitrososalicylato-derivatives of cobalt(III)[4,5] and also as nitrosalicylato-derivatives of cobalt(IV).[6-8] On exhaustive treatment with concentrated nitric acid, the bidentate salicylate ion in $[Co(en)_2(sal)]^+$ is degraded to give bidentate oxalate ion.[4] This reaction, involving contraction of the chelate ring, is more cleanly accomplished with cold acidic potassium permanganate.[9] The mechanism of this degradation has been probed in a preliminary manner by use of ^{14}C-labelling of the salicylate ion[1,9] and by use of the resolved complex.[9,10]

We now report an improved synthesis of salts of bis(ethylenediamine)salicylatocobalt(III) ion and its extension to the analogous complexes of the ligands 3-methylsalicylic, 5-methylsalicylic, and 3-hydroxy-2-naphthoic acids. Salicylato(triethylenetetramine)cobalt(III) salts have also been prepared. The spectroscopic properties of these complexes in neutral and in acidic aqueous solution have been investigated with particular regard to the site of protonation of the salicylate ligand. The scope of the degradation of co-ordinated salicylate to co-ordinated oxalate ion has also been examined.

RESULTS AND DISCUSSION

Preparation of Bis(ethylenediamine)salicylatocobalt(III) *Complexes*.—Complexes containing the ion $[Co(en)_2(sal)]^+$ were first prepared by Morgan and Main Smith[3] by three different routes: (i) replacement of ammonia by ethylenediamine in the complex $[Co(NH_3)_4(sal)]^+$; (ii) oxidation of cobalt(II) salts with hydrogen peroxide in the presence of ethylenediamine and salicylic acid; and (iii) substitution of salicylate ion in the complexes $[Co(en)_2Cl_2]^+$, $[Co(en)_2(H_2O)(OH)]^{2+}$, or $[Co(en)_2(OH)_2]^+$. However the product was contaminated with the complex $[Co(en)_3]Cl_3$ in each case except where method (iii) was applied to the dihydroxo-complex. In the latter the complex $[Co(en)_2(OH)_2]^+$ was generated in solution from *trans*-$[Co(en)_2Cl_2]Cl$ by trituration with two moles of silver(I) oxide and, after removal of silver(I) chloride, the resulting filtrate was heated with one mole of salicylic acid. Some yield was lost as the insoluble species $[Co(en)_2(salH)_2]salH$ (salH = *o*-hydroxybenzoate). This procedure has been simplified † by eliminating silver(I) oxide and maintaining the pH of the solution at *ca.* 7·5 with ammonium hydroxide solution.[4] However pH control by this method is difficult and if the medium is too acidic then the major product is $[Co(en)_2(salH)_2]salH$. By using less than the stoicheiometric quantity of salicylic acid, formation of this side product can be suppressed,[1] but at the cost of necessitating chromatographic separation (on Sephadex G10 resin) of the mixture of cobalt(III) species so produced.

We have now developed two routes for the preparation of complexes containing the $[Co(en)_2(sal)]^+$ ion which are rapid and efficient and which can be readily extended to complexes of substituted salicylate ions. The first involves reaction of the complexes *cis*- or *trans*-$[Co(en)_2Cl_2]Cl$ (1 mol) with salicylic acid (1 mol) and sodium hydroxide (2 mol). In the second method, the complex $[Co(en)_2CO_3]ClO_4$ (1 mol) is first converted to $[Co(en)_2(H_2O)_2]^{3+}$ in solution with perchloric acid (2 mol) before

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† Silver(I) salts may act as heterogeneous catalysts for stereoselective reactions of complexes (see F. P. Dwyer, A. M. Sargeson, and I. K. Reid, *J. Amer. Chem. Soc.*, 1963, **85**, 1215) and in organic reactions [*e.g.*, P. S. Walton and M. Spiro, *J. Chem. Soc.* (*B*), 1969, 42; J. M. Austin, O. D. E.-S. Ibrahim, and M. Spiro, *J. Chem. Soc.*, (*B*) 1969, 669]; therefore this reaction may have a different mechanism.

[1] Part VII, A. G. Beaumont, R. D. Gillard, and J. R. Lyons, *J. Chem. Soc.* (*A*), 1971, 1361.

[2] G. T. Morgan and J. D. Main Smith, *J. Chem. Soc.*, 1922, 1956; *ibid.*, 1923, 1096.

[3] G. T. Morgan and J. D. Main Smith, *J. Chem. Soc.*, 1924, 1996.

[4] K. Garbett and R. D. Gillard, *J. Chem. Soc.* (*A*), 1968, 979.

[5] A. G. Beaumont and R. D. Gillard, *J. Chem. Soc.* (*A*), 1968, 2400.

[6] Y. Yamamoto, K. Ito, H. Yoneda, and M. Mori *Bull. Chem. Soc. Japan*, 1967, **40**, 2580.

[7] Y. Yamamoto, M. Mori, H. Yoneda, S. Misumi, and K. Ito, *Bull. Chem. Soc. Japan*, 1969, **42**, 984.

[8] Y. Yamamoto, *Bull. Chem. Soc. Japan*, 1969, **42**, 999.

[9] A. G. Beaumont and R. D. Gillard, *J. Chem. Soc.* (*A*), 1970, 1757.

[10] R. D. Gillard and J. R. Lyons, *J. Chem. Soc.* (*A*), 1971, 2817.

treatment with salicylic acid (1 mol) and sodium hydroxide (4 mol). The perchlorate salts of the complex ions are much less soluble than the corresponding chlorides and so the products are more easily isolated by the second method.

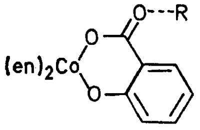
The following complexes have been prepared (those with substituted acids for the first time): $[Co(en)_2(sal)]Cl,2H_2O$, $[Co(en)_2(sal)]ClO_4,2H_2O$, $[Co(en)_2(3\text{-Mesal})]ClO_4$, [3-Mesal = 3-methylsalicylate(2-)], $[Co(en)_2(5\text{-Mesal})]Cl,2H_2O$, $[Co(en)_2(5\text{-Mesal})]ClO_4,H_2O$ [5-Mesal = 5-methylsalicylate(2-)], and $[Co(en)_2(3\text{-OHnaphth})]ClO_4$ [3-OHnaphth = 3-hydroxy-2-naphthoate(2-)]. The preparation of the latter was noticeably more difficult than the other complexes, requiring the organic acid to be added only very slowly to the solution of the other reagents. Attempted preparation of the analogous complex with 1-hydroxy-2-naphthoate ions was unsuccessful.

Comparable methods have been used to synthesise complexes in the triethylenetetramine (trien) series: $[Co(trien)(sal)]Cl,H_2O$, $[Co(trien)(sal)]ClO_4,H_2O$, and $[Co(trien)(5\text{-Mesal})]Cl,2H_2O$ were prepared from *abcf*-$[Co(trien)Cl_2]Cl$; $[Co(trien)(sal)]ClO_4,H_2O$ was also obtained from *abcd*-$[Co(trien)CO_3]ClO_4$. Samples of $[Co(trien)(sal)]ClO_4,H_2O$ obtained by the two routes had, within our experimental error, the same spectroscopic properties (electronic, i.r., and ^1H n.m.r.) despite the different geometries of the starting complexes. *X*-Ray powder photographs confirmed that the samples contained the same (one or more) crystal species; under the microscope the samples appeared homogeneous and identical. As both preparative methods allow equilibration of the complex $[Co(trien)(H_2O)_2]^{3+}$ in basic solution before addition of salicylic acid, and since under these conditions the *abcd*-geometry is preferred,[11,12] our samples of the complexes $[Co(trien)(sal)]^+$ and $[Co(trien)(5\text{-Mesal})]^+$ probably have this stereochemistry. Certainly when subjected to oxidative degradation both these complexes yielded the known *abcd*-$[Co(trien)(C_2O_4)]^+$ (see below); however this does not constitute proof of the geometry as stereochemical change could take place during degradation.

It has not been possible to obtain ^1H n.m.r. spectra of sufficient quality (at 60 MHz) to determine directly the geometry of trien in the salicylate complexes. Because salicylic acid is an unsymmetrical ligand, the complex *abcd*-$[Co(trien)(sal)]^+$ could exist in forms in which the oxygen atom of the phenol group is either *cis* (position *e*) or *trans* (position *f*) to the out-of-plane nitrogen atom (position *a*); further isomers arise from the symmetry about the secondary nitrogen atoms of the amine. Molecular models do not reveal large differences in ring strain or non-bonded interactions between the possible isomers.* Attempted isolation of the isomers of $[Co(trien)(sal)]ClO_4$ was unsuccessful, although chromatography on cation-exchange SP Sephadex C-25 resin (eluting with 0·5N-NaCl) causes incomplete separation of our samples ($\lambda_{max.}$ 517 nm) into components with $\lambda_{max.}$ 520 and 515 nm (leading and tailing fractions respectively).

The complexes synthesised in this work gave satisfactory microanalyses (for C, H, and N) and have been characterised by their i.r., electronic, and ^1H n.m.r. spectra. The degree of hydration of certain of the complexes depends upon the drying procedure; some of the water of crystallisation is lost very easily at 110 °C.[3,4]

Protonation of Co-ordinated Salicylate Ions.—The complexes $[Co(en)_2(sal)]^+$ and $[Co(NH_3)_4(sal)]^+$ form both acid and neutral series of salts,[2,3] *e.g.* $[Co(en)_2(sal)]Cl,2H_2O$ and $[Co(en)_2(sal)]Cl,HCl,3H_2O$. Morgan and Main Smith prepared many such derivatives and remarked that whereas the neutral complexes contain one molecule of firmly bound water per complex cation, the acid salts are in most cases either anhydrous or contain water which is readily removed on heating. They therefore concluded that, as one molecule of water of crystallisation or one protonated acid molecule is implicated in the complex cation, the water or hydrogen ion is located at the carbonyl oxygen and not at the hydroxylic oxygen atoms:



R = H_2O or HX

It is noteworthy that the *anhydrous* salts $[Co(en)_2(3\text{-Mesal})]ClO_4$ and $[Co(en)_2(sal)]ClO_4$, prepared in the present work, are further exceptions to the generalisation on the degree of hydration of these complexes. No further discussion of the structure of the solid protonated salts is given as the spectroscopic results detailed below refer only to the protonated species in solution.

Garbett and Gillard[4] have described the reversible changes in the electronic and circular-dichroism spectra of the $[Co(en)_2(sal)]^+$ ion on protonation in dilute mineral acids. We now report the changes in the electronic spectrum of several substituted and unsubstituted salicylato-complexes in perchloric acid solution (Table 1). The behaviour of the salicylate and methylsalicylate complexes is very similar. In *ca.* 1M acid the long wavelength *d–d* band was shifted to shorter wavelengths by *ca.* 7 nm relative to its position in neutral solution; the change in intensity was very slight. The shift in the short wavelength band was greater, *ca.* 25 nm to longer wavelengths, and was accompanied by a small increase in intensity. The shift in this latter band has been used to determine the p*K* of protonation of the

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* Recently all possible isomers in the analogous system $[Co(trien)(glycinate)]^{2+}$ were separated (R. J. Dellaca, V. Janson, W. T. Robinson, D. A. Buckingham, L. G. Marzilli, I. E. Maxwell, K. R. Turnbull, and A. M. Sargeson, *J.C.S. Chem. Comm.*, 1972, 57).

[11] A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, 1967, **6**, 787.

[12] E. Kyuno, L. J. Boucher, and J. C. Bailar, *J. Amer. Chem. Soc.*, 1965, **87**, 4458; E. Kyuno and J. C. Bailar, *ibid.*, 1966, **88**, 1120.

complexes $[Co(en)_2(sal)]^+$ (1·1 ± 0·3),[*] $[Co(en)_2(3\text{-}Mesal)]^+$ (1·3 ± 0·3), and $[Co(en)_2(5\text{-}Mesal)]^+$ (1·1 ± 0·3). In more strongly acid solutions (*e.g.* 10N-$HClO_4$ or -H_2SO_4) the complexes were unstable: a large and irreversible decrease in intensity occurred and the solutions slowly turned brownish-red. The complex $[Co(en)_2(3\text{-}OHnaphth)]ClO_4$ was unstable even in *ca.* 1M acid, depositing a dark brown solid and showing a spectrum which was featureless in the region around 500 nm. A neutral solution showed a spectrum comparable to that of the simpler salicylate complexes, although the shorter wavelength absorption band was *ca.* 20 nm to longer wavelengths.

TABLE 1

Electronic spectra of salicylate complexes in neutral and in acidic aqueous solution

Complex	$[HClO_4]$/N	$\lambda_{max.}$/nm (ε/l mol^{-1} cm^{-1})
$[Co(en)_2(sal)]Cl$	0	516 (212), 330 (2800)
	0·5	509 (220), 352 (2940)
	3	509 (219), 354 (3100)
$[Co(en)_2(3\text{-}Mesal)]ClO_4$	0	518 (237), 335 (3830)
	0·5	510 (240), 359 (3930)
	3	510 (243), 360 (4120)
$[Co(en)_2(5\text{-}Mesal)]Cl$	0	520 (242), 338 (3240)
	0·8	514 (249), 362 (3260)
	5	514 (262), 362 (3220)
$[Co(trien)(sal)]ClO_4$	0	517 (269), 331 (3160)
	0·8	510 (267), 354 (3440)
	5	508 (268), 354 (3310)
$[Co(trien)(5\text{-}Mesal)]Cl$	0	517 (323), 339 (3680)
	4	508 (340), 364 (3910)
$[Co(en)_2(3\text{-}OHnaphth)]ClO_4$	0	520 (421), 357 (3120)
	0·8	397 (2190)
	5	404 (2290)

TABLE 2

^1H N.m.r. spectra of salicylatocobalt(III) complexes

(*a*) Chemical shifts, τ [a]

		ν_3	ν_4	ν_5	ν_6	ν_{Me}	ν_{en}
$[Co(en)_2(sal)]^+$	D_2O	2·89	2·69	3·22	2·20		7·20
	D_2SO_4	2·82	2·57	3·21	2·13		7·08, 7·12
$[Co(en)_2(3\text{-}Mesal)]^+$	D_2O		2·76	3·36	2·32	7·75	7·17, 7·23
	D_2SO_4		2·65	3·37	2·28	7·74	7·11, 7·18
$[Co(en)_2(5\text{-}Mesal)]^+$	D_2O	2·93	2·82		2·37	7·77	7·16, 7·23
	D_2SO_4	2·86	2·67		2·31	7·77	7·10, 7·20
$[Co(en)_2(3\text{-}OHnaphth)]^+$ [b]	D_2O	2·51			1·52		7·19

(*b*) Coupling constants (*J*/Hz) [c]

		J_{34}	J_{35}	J_{36}	J_{45}	J_{46}	J_{56}
$[Co(en)_2(sal)]^+$	D_2O	8·3	0·8	<0·5	7·1	1·8	7·8
	D_2SO_4	8·6	1·1	<0·8	7·0	1·9	8·1
$[Co(en)_2(3\text{-}Mesal)]^+$	D_2O				6·9	1·4	7·9
	D_2SO_4				6·7	1·3	8·0
$[Co(en)_2(5\text{-}Mesal)]^+$	D_2O	8 9		<0·6		2 5	
	D_2SO_4	8·8		<0·9		2·2	

[a] Relative to internal t-butyl alcohol, τ 8·72. Values are accurate to τ ±0·01. [b] Resonances for the substituent benzene ring are highly split and therefore weak, thus accurate values cannot be reported. [c] Values are accurate to ±0·3 Hz.

I.r. spectra of solutions of the complex $[Co(en)_2(sal)]Cl$ in D_2O and in 2N-D_2SO_4 were recorded. In the region 1500—2000 cm^{-1}, the solutions showed bands at 1573 and 1608 cm^{-1}, and at 1588 and 1618 cm^{-1} respectively. If the site of protonation were the carbonyl oxygen atom, a significant change in the carboxyl group stretching vibrations might occur. The result is not conclusive, but shifts of such small magnitude suggest that protonation at the carboxyl group is unlikely. The difficulty in obtaining a good crystalline sample of a salt of the acid series precluded comparison of the i.r. spectra of solid samples (application of the literature method [3,4] gave only hygroscopic red gums).

Studies on the pH dependence of the ^1H n.m.r. spectra of mono- [13] and bis-(dipeptide) [14] complexes of cobalt(III) have readily disclosed the site of protonation; the spectra are simple and large changes (up to 0·6 p.p.m.) occur on protonation. The complex $[Co(en)_2(sal)]^+$ showed a complicated ABCX n.m.r. spectrum, although assignment of the resonances is fairly easy and it can be analysed approximately as an ABMX system. The spectrum of sodium *o*-hydroxybenzoate has been assigned [15] on a first-order basis by comparison with that of methyl *o*-hydroxybenzoate,[16] although neither are truly first order. The chemical shifts observed for co-ordinated salicylate ion (τ 2·89, 2·69, 3·22, and 2·20 for H_3, H_4, H_5, and H_6 respectively) compare well with those of sodium *o*-hydroxybenzoate (τ 2·91, 2·52, 3·07, and 2·02) even though larger shifts of H_3 and H_6 might have been expected on co-ordination.

On acidification the n.m.r. spectrum of the complex $[Co(en)_2(sal)]^+$ changed slightly (Table 2). The resonances of H_3 and H_6 moved downfield by 0·07 and 0·065 p.p.m. respectively; no significant shift was observed for H_5 and the largest shift of all was observed

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[*] This result may be compared with the value of 1·8 based on small changes in the circular-dichroism spectrum.[4] The difference is unexpectedly large and may reflect the greater sensitivity of c.d. spectra (as compared with electronic or ^1H n.m.r. spectra) to small changes in the environment of the chromophore, *e.g.* as the result of ion pairing.

[13] I. G. Browning, R. D. Gillard, J. R. Lyons, P. R. Mitchell, and D. A. Phipps, *J.C.S. Dalton*, 1972, 1815.

[14] R. D. Gillard and P. R. Mitchell, unpublished work.

[15] G. Stein and M. Tomkiewicz, *Trans. Faraday Soc.*, 1970, **66**, 517.

[16] R. Freeman, N. S. Braeca, and C. A. Reilly, *J. Chem. Phys.*, 1963, **38**, 293.

for H_4. Protonation of the complexes $[Co(en)_2(3\text{-}Mesal)]^+$ and $[Co(en)_2(5\text{-}Mesal)]^+$ also caused the greatest change in the H_4 resonance, but in the latter complex the shift in the H_3 resonance (0·07 p.p.m.) was again slightly greater than that of H_6 (0·06 p.p.m.). It is therefore concluded that the site of protonation is the oxygen atom of the phenol group rather than that of the carboxyl group (using the argument that resonances nearest to the site of protonation suffer the greatest change). Unexpected long-range interaction between H_4 and the proton of the phenol group in methyl *o*-hydroxybenzoate has been observed (J = 0·4 Hz for a five-bond coupling constant).[16] No such coupling could be observed in the spectrum of co-ordinated salicylate ion as the width at half-height of individual peaks was at least 1 Hz, but the large change in the chemical shift of H_4 on protonation of the oxygen atom of the phenol group may be in some way related.

TABLE 3

Summary of results on the degradation of salicylatocobalt(III) and allied complexes

Substrate	Oxidant	Product	Ref.
$[Co(NH_3)_4(sal)]^+$	$H^+/KMnO_4$	*a*	*b*
$[Co(en)_2(sal)]^+$	Conc. HNO_3	$[Co(en)_2(C_2O_4)]^+$ [c]	4
	$H^+/KMnO_4$	$[Co(en)_2(C_2O_4)]^+$ [d]	9
	H_2O_2/H^+ or H_2O_2	*a*	*b*
	Ce^{4+}/H_2SO_4	*a*	*b*
	HOCl	*a*	*b*
$[Co(en)_2(3\text{-}Mesal)]^+$	Conc. HNO_3	$[Co(en)_2(C_2O_4)]^+$	*b*
	$H^+/KMnO_4$	$[Co(en)_2(C_2O_4)]^+$	*b*
$[Co(en)_2(5\text{-}Mesal)]^+$	Conc. HNO_3	$[Co(en)_2(C_2O_4)]^+$	*b*
	$H^+/KMnO_4$	$[Co(en)_2(C_2O_4)]^+$	*b*
$[Co(en)_2(5\text{-}NO_2sal)]^+$	Conc. HNO_3	$[Co(en)_2(C_2O_4)]^+$	4
$[Co(en)_2(3\text{-}OHnaphth)]^+$	Conc. HNO_3	*a*	*b*
	$H^+/KMnO_4$	$[Co(en)_2(C_2O_4)]^+$	*b*
$[Co(trien)(sal)]^+$ [e]	$H^+/KMnO_4$	*abcd*-$[Co(trien)(C_2O_4)]^+$	*b*
$[Co(trien)(5\text{-}Mesal)]^+$	$H^+/KMnO_4$	*abcd*-$[Co(trien)(C_2O_4)]^+$	*b*
$[Co(en)_2(pic)]^{2+}$	Conc. HNO_3	$[Co(en)_2(pic)]^{2+}$ [f]	*b*
	$H^+/KMnO_4$	$[Co(en)_2(pic)]^{2+}$ [f]	*b*

[a] Complex decomposes. [b] This work. [c] Product has racemised and lost C(7). [d] Product retains configuration of reactant; C(1), C(2), and C(7) are retained in the product to the extent of 50, 100, and 0% respectively. [e] Probably the *abcd*-isomer. [f] The complex is recovered unchanged from the reaction medium.

The dependence of the ^1H n.m.r. spectrum of the complex $[Co(en)_2(5\text{-}Mesal)]^+$ upon pH was studied in order to determine the pK of protonation {the spectrum of the complex $[Co(en)_2(sal)]^+$ is too complicated for detailed study}. Although the spectrum was decidedly second order (ABX), it can be interpreted fully and the measured values of the coupling constants corrected[17] using a parameter $z = \delta\nu_{AB}/[(\delta\nu_{AB})^2 + J_{AB}{}^2]^{\frac{1}{2}}$. Plots of ν_3, ν_4, ν_6, δ_{34} and the coupling constants against pH gave a value of 2·1 ± 0·05 for the pK of protonation (in D_2O). Two solutions of the complex in H_2O were remeasured to give the pK (in H_2O) as 1·4 ± 0·1 (*cf.* the value of 1·1 ± 0·3 obtained from changes in the electronic spectrum).

Oxidative Degradation of Co-ordinated Salicylate Ion.—Treatment of the complex $[Co(en)_2(sal)]^+$ with a small amount of concentrated nitric acid gave a mixture containing the brown complex $[Co(en)_2(5\text{-}NO_2salH)]^{2+}$ and green paramagnetic materials; an excess of nitric acid yielded only the former and prolonged heating with an excess of concentrated nitric acid gave the complex $[Co(en)_2(C_2O_4)]^+$.[4-8] Intense green colours were also given by the complexes $[Co(en)_2(3\text{-}Mesal)]^+$ and $[Co(trien)(sal)]^+$ on treatment with a small quantity of nitric acid, but not by those complexes containing alkyl substituents at the 5-position. With an excess of nitric acid all the substituted salicylate complexes gave brown solutions. On exhaustive treatment with this reagent the complex $[Co(en)_2(3\text{-}OHnaphth)]^+$ underwent decomposition, while those of $[Co(en)_2(3\text{-}Mesal)]^+$ and $[Co(en)_2(5\text{-}Mesal)]^+$ gave, after work up, solutions containing the complex $[Co(en)_2(C_2O_4)]^+$, identified from its electronic spectrum. As was found for the unsubstituted complex,[9] this degradation yielding co-ordinated oxalate ions is more conveniently carried out with acidic potassium permanganate. The complexes $[Co(en)_2(3\text{-}Mesal)]^+$, $[Co(en)_2(5\text{-}Mesal)]^+$, $[Co(en)_2(3\text{-}OHnaphth)]^+$, $[Co(trien)(sal)]^+$, and $[Co(trien)(5\text{-}Mesal)]^+$ may each be degraded in this way. The products were identified as the perchlorate salts of $[Co(en)_2(C_2O_4)]^+$ and of *abcd*-$[Co(trien)(C_2O_4)]^+$ by comparison of electronic and i.r. spectra with those of authentic specimens.

The action of acidified potassium permanganate on the complex $[Co(NH_3)_4(sal)]^+$ led to extensive decomposition and no oxalato-complex was identified among the products. It seems that the stability conferred by chelating amines is necessary to prevent decomposition under such vigorous reaction conditions.

The complexes which have so far been converted to

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[17] J. Dyer and J. Lee, *Trans. Faraday Soc.*, 1966, **62**, 257.

oxalato-products are collected in Table 3 for ease of reference. Attempts to extend the range of the degradation yielded only negative results. The complex $[Co(en)_3][Co(sal)_3]$ has been reported as an insoluble powder.[18] This is the only known salicylatocobalt(III) complex not belonging to the series $[CoN_4(sal)]_4{}^+$; we were unable to prepare a good sample. The complexes $[Co(en)_2(phthalate)]^+$ and $[Co(en)_2(homophthalate)]^+$ have been reported [19] but are difficult to isolate except as gums; [20,21] that of $[Co(en)_2(anthranilate)]^{2+}$ is unknown. The complex $[Co(en)_2(pic)]^{2+}$ (pic = pyridine-2-carboxylate) [22] can be recovered unchanged from both acidic potassium permanganate solution and boiling concentrated nitric acid.

EXPERIMENTAL

Spectra were recorded on the following instruments: Unicam SP 500 and 800 B (electronic); Perkin-Elmer 137 (i.r.) and R10 (^{1}H n.m.r. at 60 MHz and 14,092 gauss).

Preparation of Complexes.—Salicylic acid (Reagent grade) and 3-hydroxy-2-naphthoic acid (Koch–Light) were used directly. 3-Methylsalicylic acid (2-hydroxy-*m*-toluic acid, Hopkin and Williams, Reagent grade) and 5-methylsalicylic acid (Aldrich Chemical Co. Ltd.) were first recrystallised from hot water. Two methods were used for preparation of complexes of the ethylenediamine series. (i) The complex *trans*-$[Co(en)_2Cl_2]Cl$ (10 g) dissolved in water (80 cm^3) was treated with sodium hydroxide (2·8 g) and then salicylic (4·84 g) or methylsalicylic acid (5·32 g) was added slowly with stirring. The mixture was warmed on a steam bath for about 30 min, filtered, and allowed to crystallise slowly at room temperature. The product was recrystallised at least once from water, washed with methylated spirits and with ether, and dried at 110 °C for 3 h. (ii) To a solution of the complex $[Co(en)_2(CO_3)]ClO_4$ (5·0 g) in water (40 cm^3) was added, dropwise with stirring, just sufficient concentrated perchloric acid to neutralise the carbonate ions. Sodium hydroxide (2·36 g) and salicylic (2·04 g), methylsalicylic (2·25 g), or hydroxynaphthoic acid (2·78 g) were added and the procedure of method (i) thereafter followed.

Complexes of the triethylenetetramine series were similarly synthesised from the complexes *abcf*-$[Co(trien)Cl_2]Cl$ and *abcd*-$[Co(trien)CO_3]ClO_4$, which were obtained by literature methods.[11] The complex $[Co(trien)(sal)]Cl$, prepared from the dichloro-complex, was converted to the perchlorate salt by anion exchange on Deacidite FFIP resin.

Table 4

Microanalytical data

Complex	Found (%) C	Found (%) H	Found (%) N	Calc. (%) C	Calc. (%) H	Calc. (%) N
$[Co(en)_2(sal)]ClO_4$	31·4	5·0	13·4	31·85	4·85	13·5
$[Co(en)_2(3\text{-}Mesal)]ClO_4$	33·4	5·1	13·0	33·6	5·15	13·05
$[Co(en)_2(5\text{-}Mesal)]Cl,2H_2O$	35·8	7·0	13·8	35·95	6·55	14·0
$[Co(en)_2(5\text{-}Mesal)]ClO_4,H_2O$	32·2	5·0	12·6	32·25	5·40	12·55
$[Co(en)_2(3\text{-}OHnaphth)]ClO_4$	38·5	4·8	11·7	38·75	4·75	12·05
$[Co(trien)(sal)]Cl,H_2O$	39·8	6·2	14·4	39·55	6·10	14·2
$[Co(trien)(sal)]ClO_4,H_2O$	34·2	5·4	12·4	34·05	5·25	12·2
$[Co(trien)(5\text{-}Mesal)]Cl,2H_2O$	39·6	6·8	13·3	39·4	6·60	13·15

Microanalytical results for the complexes are reported in Table 4. I.r. data are listed in Supplementary Publication. No. SUP 20585 (1 p., 1 microfiche).*

X-Ray Powder Data.—Samples of the complex $[Co(trien)(sal)]ClO_4,H_2O$, prepared by different routes, had the following *d*-spacings determined using Cu-K_α radiation: 794, 639, 545 (strong), 505, 419 (strong), 386 (weak), 350, 315, 290 (weak) pm (±3 pm).

I.r. Spectra of the Complex $[Co(en)_2(sal)]^+$ *in Solution.*—A solution of the complex $[Co(en)_2(sal)]Cl,2H_2O$ in D_2O was evaporated to dryness *in vacuo* at 30 °C in order to exchange the protons on the amine nitrogen atoms and so eliminate the broad N–H bending vibration from the spectrum. Solutions of the N-deuteriated complex (100 mg) in D_2O (1 cm^3) or in 2·2N-D_2SO_4 (1 cm^3) were examined using a liquid cell with silver iodide windows and path length of 0·025 mm.

^{1}H *N.m.r. Spectra.*—The residual HDO peak in D_2O solutions was minimised by dissolving the complexes in warm D_2O (99·7%) and evaporating to dryness *in vacuo*, thus exchanging the ethylenediamine N–H protons and replacing the H_2O of crystallisation. In some strongly acidic solutions, in which the residual HDO peak (or its spinning side bands) overlapped with the higher-field aromatic resonances, a second exchange was necessary. Solutions of the complexes (10—15%, *i.e.* 0·1—0·2M) were acidified with D_2SO_4 (10^{-3}, 10^{-1}, or 5M). The anhydrous D_2SO_4 used in these experiments was prepared by redistillation of freshly distilled SO_3 into D_2O (99·7%). The pH of solutions used for n.m.r. measurements were determined using a Radiometer pH 4 instrument; the sample was contained in a 1 cm^3 beaker fitted with a Radiometer g222c glass electrode and a K100 calomel electrode with a modified tip. Recorded pD values were corrected for the response of the glass electrode in D_2O using the equation: [23]

$$\text{true pD} = 0{\cdot}40 + \text{pH measured in } D_2O$$

The true p*K* for protonation of the complex $[Co(en)_2(5\text{-}Mesal)]^+$ was determined from measurements of the ^{1}H n.m.r. spectrum and pH of two aqueous solutions whose pH had been adjusted approximately to the p*K* calculated from the results in D_2O.

Oxidative Degradation of Salicylate Ion.—Experimental procedures using concentrated nitric acid [4] and acidic

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are supplied as full size copies).

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potassium permanganate[9] have been described previously. The following amended method was used for potassium permanganate oxidations. The perchlorate salt of the salicylate complex (2·0 g) in 0·5N-perchloric acid (100—300 cm^3, depending on the solubility) was treated with a saturated solution of potassium permanganate (8·0 g). The resulting mixture was stirred at room temperature for 10 min, during which time the temperature of the solution increased, there was a vigorous evolution of gas (CO_2), and manganese dioxide was precipitated. After filtration the solution was neutralised, if necessary, with potassium carbonate and then passed down an anion-exchange column in the perchlorate form to remove the excess of permanganate ions. The solution was concentrated on a water bath and most of the sparingly soluble potassium perchlorate was removed by crystallisation. Further crystallisation yielded a mixture of potassium perchlorate and the perchlorate salt of the cobalt(III) complex, which were separated by using the density difference between these two materials when suspended in methanol or ethanol.

Products were identified by electronic and i.r. spectra. For the purpose of comparison, perchlorate salts of the complexes $[Co(en)_2(C_2O_4)]^+$ and *abcd*-$[Co(trien)(C_2O_4)]^+$ were prepared.[4, 23] The major peaks in the i.r. spectra are $[Co(en)_2(C_2O_4)]ClO_4$: 3280, 3220, 3110, 1700, 1655, 1575, 1408, 1273, 1100 (broad), 1060, 1000, 930, 805, 720, 620, 595, 530, and 490; *abcd*-$[Co(trien)(C_2O_4)]ClO_4$: 3280, 3220, 1700, 1675, 1655, 1605, 1580, 1400, 1260, 1075 (broad), 800, 720, 625, 565, and 480 cm^{-1}. The electronic spectrum of the former presents no difficulties,[4] but we summarise in Table 5 our results and data in the literature for the isomers of the latter complex.

TABLE 5

Electronic spectra of the complex $[Co(trien)(C_2O_4)]^+$

Complex	Counter ion	$\lambda_{max.}$/nm	Relative $\varepsilon_{max.}$	Ref.
abcf		357, 493	1·12	*a*
abcf	NO_3^-	358, 493	1·29	12
abcd		357, 497	1·00	*a*
abcd	NO_3^-	357, 497	1·05	12
abcd	ClO_4^-	357, 497	1·06	*b*
abcd [c]	ClO_4^-	357, 497	1·10	*b*
Product of degradation of salicylate complex [c]	ClO_4^-	357, 497	1·11	*b*
Product of degradation of 5-Mesal complex [c]	ClO_4^-	356, 496	1·18	*b*

[a] G. R. Brubaker and D. P. Schaefer, *Inorg. Chem.*, 1971, **10**, 968. [b] This work. [c] In the presence of an excess of perchlorate ions.

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