Water-soluble Cobalt(II) Complexes of *NN'*-Substituted Bis(salicylaldimine-5-sulphonic Acids). Oxygen-carrying Properties and Conversion into Cobalt(III) Organometallic Compounds

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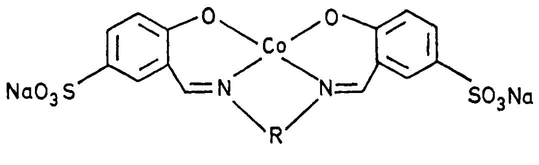
The cobalt(II) complexes of a series of *NN'*-substituted bis(salicylaldiminesulphonic acids) L = $^{-}O_3SC_6H_3(O^-)-CH{=}N-R-N{=}CH-(O^-)C_6H_3SO_3^-$ with R = $(CH_2)_2$, $(CH_2)_3$, $CH_2CH(CH_3)$, and *o*-C_6H_4 have been prepared as water-soluble sodium salts, $Na_2[CoL]$. Apart from the spin-free $(CH_2)_3$ complex, the remaining spin-paired compounds can be converted into water-soluble organometallic cobalt(III) derivatives. The same cobalt(II) compounds also react readily with oxygen at room temperature to yield mixtures of the superoxo-type $[CoL(O_2)(OH_2)]$ and peroxo-type $[\{CoL(OH_2)\}_2(O_2)]$ complexes. The formation of superoxo-type species is reversible at room temperature while the peroxo-species require higher temperatures for dissociation. In the solid state $Na_2[Co(SO_3\text{-salen})]$ [SO_3-salen = *NN'*-ethylenebis(salicylaldimine-5-sulphonate)] and its ethylenediamine adduct also react to form complexes of the superoxo-type.

A NUMBER of quadridentate salicylaldimine cobalt(II) complexes have been found to behave as reversible oxygen carriers.[1] Such metal complexes have attained some importance in model studies on the biologically significant reaction of oxygen carrying. Similar cobalt(II) compounds have also been used as the starting point for the synthesis of organometallic derivatives of Co^{III}, which have some formal similarity with vitamin B_{12} biochemical organometallic species.[2] One of the experimental disadvantages in such model studies has been the fact that the synthetic compounds are usually insoluble in water, the normal biological medium.

Metal complexes derived from salicylaldehyde-5-sulphonic acid [3] and related imino-derivatives [4] have been shown to be soluble in water and this paper reports a study of the synthesis of the cobalt(II) complexes derived from *NN'*-substituted bis(salicylaldimine-5-sulphonates) (1) {R = $(CH_2)_2$, $Na_2[Co(SO_3\text{-salen})]$; R = $(CH_2)_3$, $Na_2[Co(SO_3\text{-sal-1,3-pn})]$; R = $CH_2CH(CH_3)$, $Na_2[Co(SO_3\text{-sal-1,2-pn})]$; R = *o*-$C_6H_4$, $Na_2[Co(SO_3\text{-salphen})]$} and related cobalt(III)-alkyl derivatives. The reactivity of the cobalt(II) complexes towards oxygen in aqueous solution and the solid state has also been examined using e.s.r. spectroscopy as the structural probe.



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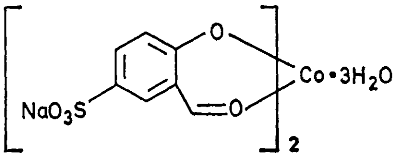
RESULTS AND DISCUSSION

Synthesis of Cobalt(II) *Complexes.*—A satisfactory route to the synthesis of the quadridentate complexes of Co^{II} which avoids the need to prepare each ligand independently results from the reaction of an appropriate diamine with the preformed cobalt(II) complex derived from the disodium salt of salicylaldehyde-5-sulphonic acid (2). This latter complex was first reported by Calvin and Melchior.[3] It has a magnetic moment of 4.69 B.M.† at room temperature, a value somewhat between that normally found for high-spin cobalt(II) compounds with six-co-ordinate and those with four-co-ordinate geometries. It is uncertain whether two of the water molecules are associated with Co^{II} or with the Na^+ ions. The corresponding salicylaldehyde–cobalt(II) complex has been isolated [5] as a dihydrate having a moment of 4.74 B.M.



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Complex (2) reacts readily with diamines to form the quadridentate complexes (1) in refluxing ethanol. The complexes are all isolated as hydrates. The room-temperature magnetic moments of three of the complexes are similar to those found for the parent salicylaldimine compounds and indicate a typical square-planar co-ordination mode about the metal (Table 1). The 1,3-propylenedi-imine complex is high spin, as are both the hydrated and anhydrous forms of the parent complex [Co(sal-1,3-pn)].[6] The latter complex is presumed to have a non-planar (tetrahedral) arrangement of the ligand about Co^{II} and this also appears appropriate for the sulphonate derivative.

When $Na_2[Co(SO_3\text{-sal})_2]$ reacts with a greater than two-fold excess of ethylenediamine (en) or when $Na_2[Co(SO_3\text{-salen})]$ reacts with a further mol of the diamine a compound is isolated whose analysis corresponds with the empirical formula $Na_2[Co(SO_3\text{-salen})]\cdot NH_2CH_2CH_2NH_2$. The i.r. spectrum of the complex shows sharp absorption bands assignable to N–H stretching vibrations at 3 250, 3 185, and 3 120 cm^{-1}. The method of synthe-

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† Throughout this paper: 1 B.M. = 9.274×10^{-24} A m^2; 1 G = 10^{-4} T.

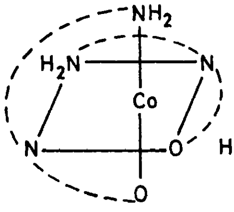
TABLE 1

Microanalytical data and room-temperature magnetic moments

Complex	μ_{293}/B.M.	Analysis (%) Found C	H	N	S	Calc. C	H	N	S
$Na_2[Co(SO_3\text{-salen})]\cdot 2H_2O$	2.81	33.5	2.5	5.1	10.7	34.0	2.9	5.0	11.3
$Na_2[Co(SO_3\text{-sal-1,2-pn})]\cdot 2H_2O$	2.68	34.9	3.2	4.7	10.8	35.2	3.1	4.8	11.0
$Na_2[Co(SO_3\text{-sal-1,3-pn})]\cdot 5H_2O$	4.59	32.5	3.0	4.3	10.4	32.2	4.1	4.4	10.1
$Na_2[Co(SO_3\text{-salphen})]\cdot 6H_2O$	2.78	35.2	2.7	3.9	9.6	35.3	3.5	4.1	9.4
' $Na_2[Co(SO_3\text{-salen})]\cdot en\cdot 2H_2O$ '	2.57	34.4	3.0	7.3	10.3	34.6	3.9	9.0	10.3
$Na_2[Co(SO_3\text{-sal})_2]\cdot 3H_2O$	4.69	29.6	3.0		10.1	30.1	2.5		11.5
$Na_4[\{Co(SO_3\text{-salen})\}_2(O_2)]\cdot 10H_2O$	dia.*	30.2	3.1	4.2	9.6	30.2	3.5	4.4	10.1
$Na_4[\{Co(SO_3\text{-salen})(imH)\}_2(O_2)]\cdot 12H_2O$	dia.	31.1	3.0	7.7	8.5	31.6	3.3	7.8	8.9
$Na_2[CoMe(SO_3\text{-salen})]\cdot 5H_2O$	dia.	32.3	3.7	4.5	10.5	32.2	4.0	4.4	10.1
$Na_2[CoEt(SO_3\text{-salen})]\cdot 4H_2O$	dia.	34.3	3.9	4.6	9.7	34.3	4.0	4.4	10.2
$Na_2[CoPr^n(SO_3\text{-salen})]\cdot 5H_2O$	dia.	34.6	3.6	4.0	9.4	34.5	4.4	4.2	9.7
$Na_2[CoEt(SO_3\text{-sal-1,2-pn})]\cdot 6H_2O$	dia.	33.4	3.5	4.3	9.5	33.5	4.6	4.1	9.4
$Na_2[CoMe(SO_3\text{-salphen})]\cdot 6H_2O$	dia.	35.3	2.7	4.1	9.0	36.1	3.9	4.0	9.1

* dia. indicates the complex is either diamagnetic or has a small temperature-independent paramagnetic contribution.

sis is known to produce tridentate salicylaldimine ligands in similar reactions involving other metals [7] and solution studies [8] on the reactions of iron(III) with salicylaldehyde-5-sulphonate ions and ethylenediamine have claimed to have demonstrated that such a ligand is formed at least *in situ*, so that an alternative formulation for the present complex would be as the bis-*N*-2-aminoethylsalicylaldimine compound. Such a complex would be expected to show either six-fold co-ordination (3) or five- or four-fold co-ordination with one or neither of the NH_2 groups of the 2-aminoethyl substituents being co-ordinated (4). Any one of these three types of complex would be expected to contain high-spin Co^{II} and show a moment in the range 4.5—5.1 B.M. On present knowledge,[1] such complexes would not be expected to react reversibly with dioxygen although each complex might well oxidise irreversibly to a cobalt(III) derivative.



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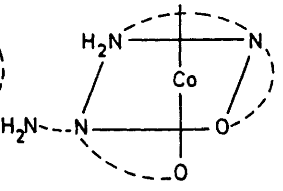

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The complex reported here contains low-spin Co^{II} (Table 1) and reacts reversibly with oxygen both in solution and the solid state, suggesting that the complex contains the SO_3-salen ligand co-ordinated to Co together with an additional ethylenediamine molecule also co-ordinated to Co^{II}.

Synthesis of Cobalt(III) *Organometallic Compounds*.—The compound $Na_2[Co(SO_3\text{-salen})]$ is readily reduced by $Na[BH_4]$ in alkaline aqueous ethanol to give a deep green product which reacts rapidly with added MeI, EtI, or Pr^nI to form the organometallic species $[Co^{III}R(SO_3\text{-salen})]^{2-}$, R = Me, Et, or Pr^n. The sodium salts are quite soluble in water but sparingly soluble in alcohols and most common organic solvents. The analogous organometallic complexes $[CoMe(SO_3\text{-salphen})]^{2-}$ and $[CoMe(SO_3\text{-sal-1,2-pn})]^{2-}$ have been similarly prepared and are also water soluble. The complexes decomposed upon continued exposure to visible light forming hydrocarbons and the corresponding cobalt(II) complex in the absence of air. The cobalt(II) species were detected using e.s.r. spectroscopy. In the presence of air the soluble peroxo-species are formed by further reaction of the cobalt(II) complexes with dioxygen.

Oxygenation Reactions in Aqueous Dimethylformamide Solution.—A solution of $Na_2[Co(SO_3\text{-salen})]$ in a carefully deoxygenated mixture of water and dimethylformamide (dmf) shows an e.s.r. spectrum at 120 K having a line shape characteristic of a tetragonally distorted, low-spin d^7 cobalt(II) species $[Co(chelate)L'_n]$ ($n = 1$ or 2) in which the odd electron occupies a d_{z^2} orbital [9-11] (Figure 1); the g and A values were deduced by computer simulation of the spectrum [12] and are listed in Table 2. A linewidth dependence on the nuclear quantum number m_I was not included in the fitting [12] which explains why the high-field z lines are narrower than those observed. The co-ordinated ligand L′ may be either water or dmf. Similar spectra are given by the 1,2-pn and *o*-phenylene derivatives. The addition of an excess of imidazole (*i.e.* greater than 1 : 1 molar equivalents) to the solution of $Na_2[Co(SO_3\text{-salen})]$ causes a splitting of the z lines into triplets by ^{14}N superhyperfine coupling, indicative of the co-ordination of one imidazole molecule (imH) to Co^{II}. This is shown in Figure 2 where it can also be seen that small changes occur in the x and y regions. A solid complex of analytical composition $Na_2[Co(SO_3\text{-salen})]\cdot 0.5imH$ could be recrystallised from such solutions.

The e.s.r. spectrum of $Na_2[Co(SO_3\text{-salen})]$ measured in frozen dmf–water in the presence of a small excess of pyridine also indicates co-ordination of 1 mol of ligand while in the presence of a large excess the spectrum shows splitting of some of the z lines into quintets, indicating the attachment of two pyridine molecules at least at low temperatures (Figure 3). In this spectrum the x region

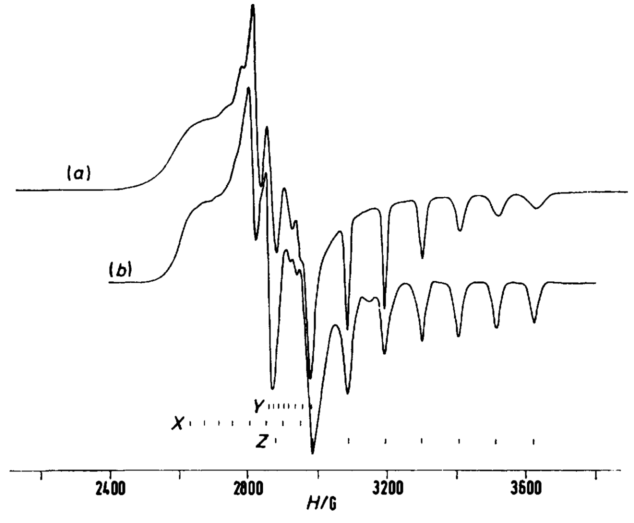


FIGURE 1 E.s.r. spectrum of $Na_2[Co(SO_3\text{-salen})]$ in frozen (deoxygenated) dmf–water, 120 K. (*a*) Observed spectrum, (*b*) computer-simulated spectrum (microwave frequency 9 146 MHz)

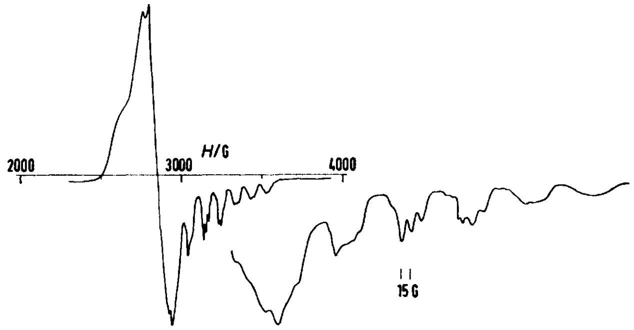


FIGURE 2 E.s.r. spectrum of $Na_2[Co(SO_3\text{-salen})]$ in frozen (deoxygenated) dmf–water in the presence of excess of imidazole. ^{14}N hyperfine splitting of the *z* lines due to a mono(imidazole) adduct (microwave frequency 9 154 MHz)

becomes narrower than that in Figure 1 on account of a lower A_x value. This effect has previously been noted in five- and six-co-ordinate pyridine adducts of [Co(salen)].[13] In general the present *g* and *A* parameters given in Table 2 are similar to those of the unsulphonated [Co(salen)L′] species indicating essentially similar electronic environments around cobalt.

When oxygen is admitted to a solution of $Na_2[Co(SO_3\text{-salen})]$ in dmf–water and the e.s.r. spectrum recorded at 120 K, the normal d_{z^2} electron signal is found to have diminished in intensity by a factor of *ca.* 10^3. This is estimated to involve oxygenation of *ca.* 80% of the complex. There is also a weak signal of the type recorded for cobalt(III) superoxo-type complexes formed from $[Co^{II}(salen)]$ and related molecules in the presence of a Lewis base L′ such as pyridine.[1,10,13] This superoxo-complex may be represented as $Na_2[Co(SO_3\text{-salen})(O_2)L']$. The initial e.s.r. spectrum of the starting complex as measured at 120 K cannot be regenerated by bubbling N_2 gas through the solution at room temperature. However, after carrying out such a procedure at 100 °C, the e.s.r. spectrum is completely returned. This indicates that a reversible oxygenation

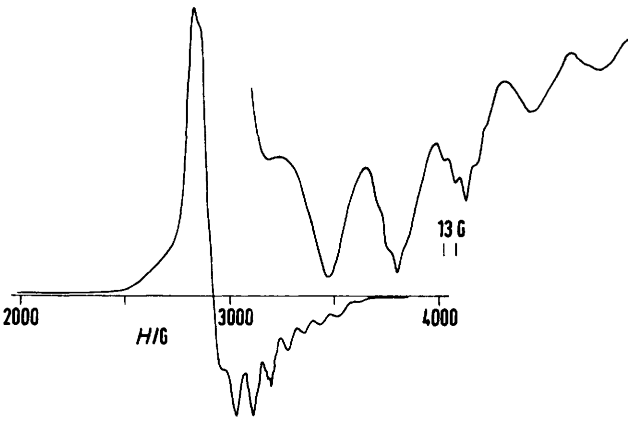
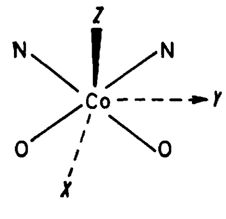


FIGURE 3 E.s.r. spectrum of $Na_2[Co(SO_3\text{-salen})]$ in frozen (deoxygenated) dmf–water in the presence of a large excess of pyridine, indicating formation of a dipyridine adduct (microwave frequency 9 148 MHz)

TABLE 2

E.s.r. parameters for axially solvated cobalt(II) quadridentate complexes [a]



Complex	g_x	g_y	g_z	$10^{-4}A_x^{Co}$	$10^{-4}A_y^{Co}$ cm^{-1}	$10^{-4}A_z^{Co}$
$Na_2[Co(SO_3\text{-salen})]\cdot 2H_2O$ [b]	2.335	2.23	2.005	50	17.5	100
	±0.005	±0.005	±0.005	±2	±2	±1
$Na_2[Co(SO_3\text{-sal-1,2-pn})]\cdot 2H_2O$ [c]	2.40	2.23	2.03	50	17	100
$Na_2[Co(SO_3\text{-salphen})]\cdot 3H_2O$ [c]	2.34	2.23	2.02	50	17	98
$Na_2[Co(SO_3\text{-salen})]\cdot en\cdot 2H_2O$ [c,d]	2.34	2.23	2.01	50	17	100

[a] Measured at *X*-band frequency in frozen dmf–water at 120 K. [b] Parameters deduced by computer simulation (see Figure 1). Linewidths (G): $\sigma_x = 40$, $\sigma_y = 10$, $\sigma_z = 12.5$. Excess of imidazole yields five-co-ordinate adduct with $A(^{14}N) = 15$ G. Excess of pyridine yields six-co-ordinate adduct with $A(^{14}N) = 13$ G. [c] Parameters deduced by inspection. Estimated errors $g_i \pm 0.01$, $A_x \pm 2$, $A_y \pm 2$, $A_z \pm 1$. [d] Powder spectrum gives ^{14}N hyperfine triplets on *z* lines with $A(^{14}N) = 15$ G.

process can occur in aqueous solution similar to that observed[14] for the parent complex [Co(salen)] in the presence of Lewis bases such as pyridine to form a 2 : 1 Co–O_2 diamagnetic, peroxo-type compound $Na_4[\{Co(SO_3\text{-salen})L'\}_2(O_2)]$. The room-temperature oxygenation followed by deoxygenation at 100 °C can be cycled at least five times before the initial complex is found to have lost some activity, no doubt due to slow irreversible oxidation.

It is not possible to say whether H_2O or dmf plays the part of co-ordinated Lewis base L′ in this reaction modifying the cobalt(II) electronic configuration so as to induce reaction with oxygen. However the brown cobalt(II) complex also reacts readily with oxygen in pure water, to yield a green-brown diamagnetic compound which can be isolated from solution. It is considered to be a 2 : 1 Co–O_2 peroxo-type complex of empirical formula $Na_4[\{Co(SO_3\text{-salen})(OH_2)\}_2(O_2)]$. The i.r. spectrum of the complex is also generally similar to the parent complex except that the former shows a broad absorption band centred at 1 180 cm^{-1} in the region corresponding to S–O stretching vibrations where the latter shows single strong absorption bands at 1 230 and 1 170 cm^{-1} which are associated with such vibrations. There is no detectable band associated with O–O vibrations in the region expected for peroxo-groups, *viz.* 790—884 cm^{-1}, indicating that the symmetry of the molecule has made such vibrations i.r. inactive as reported for other binuclear cobalt–oxygen complexes.[15,16]

In the absence of a structural study it cannot be stated with certainty that each cobalt has a water molecule co-ordinated to it although this is considered highly probable in the light of the present state of knowledge of such complexes, which suggests that an appropriate Lewis base is necessary to facilitate reaction between a cobalt(II) square-planar complex and oxygen.[1]

TABLE 3

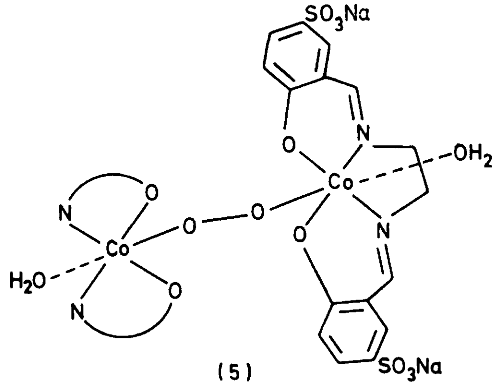
E.s.r. parameters for $[Co(SO_3\text{-salen})(O_2)L']^{2-}$ and related superoxo-type complexes [a]

Complex	g_x	g_y	g_z	$10^{-4}A_x$	$10^{-4}A_y$	$10^{-4}A_z$	Angle
					cm^{-1}		Co–O–O/°
$[Co(SO_3\text{-salen})(O_2)]^{2-}$ (powder)	Poor resolution ($g = 2.02$)				*ca.* 15		
$[Co(SO_3\text{-sal-1,2-pn})(O_2)]^{2-}$ (in dmf–water, 120 K) [b]	2.011	2.09	1.995	5.8	19.5	8.0	116
$[Co(SO_3\text{-salphen})(O_2)]^{2-}$ (in dmf–water, 120 K)	Weak signal, major product Co–O–O–Co						
$[Co(SO_3\text{-salen})(O_2)(en)]^{2-}$ (powder) [c]	2.007	2.083	1.991	7.0	17.0	9.0	116

[a] The labelling of co-ordinates and angles is as described in ref. 12. Estimated errors g_y, g_z ± 0.002; g_x ± 0.005; A_i ± 0.5; Co–O–O angle ±2°. [b] Linewidths (G): $\sigma_x = 6.5$, $\sigma_y = 10$, $\sigma_z = 7$. [c] Linewidths (G): $\sigma_x = 7$, $\sigma_y = 9$, $\sigma_z = 8$.

The ' peroxo '-complex can be recrystallised from aqueous solutions containing stronger Lewis bases such as ammonia or imidazole and the resulting compounds then contain such ligands presumably having displaced the water co-ordinated to cobalt. The complexes may also serve as intermediates for further syntheses of water-soluble cobalt(III) complexes. Thus acetylacetonate (acac) reacts with $Na_4[\{Co(SO_3\text{-salen})(OH_2)\}_2(O_2)]$ to form the water-soluble complex $Na_2[Co(SO_3\text{-salen})(acac)]$.

A number of peroxo-type binuclear complexes of [Co(salen)] with oxygen have been isolated[14] in which Lewis bases such as dmf, dimethyl sulphoxide (dmso), or pyridine are co-ordinated to Co. The constitution of such complexes with pyridine[16] and dmf[17] has been established by complete *X*-ray structural studies and a possible structure for the present complex may thus be proposed as in (5). Other water-soluble μ-peroxo-complexes containing ammine, di-imine, amino-acid, peptide, and phthalocyanine ligands are described in the review by Basolo and co-workers.[1]



(5)

The 1,2-propylenedi-imine complex $Na_2[Co(SO_3\text{-sal-1,2-pn})]$ gives an e.s.r. spectrum in oxygen-free aqueous dmf which is very similar in all respects to that of the ethylenedi-imine compound. It also reacts readily with oxygen at room temperature. However, the e.s.r. spectrum obtained both at room temperature and (with better resolution) at 120 K (Figure 4) indicates that a substantial quantity of a superoxo-type 1 : 1 Co–O_2 complex is formed with no evidence for any cobalt(II) compound remaining. This shows a qualitative distinction from the ethylenedi-imine system where the greater proportion of cobalt forms a binuclear peroxo-complex. The e.s.r. spectrum is again consistent with a sixth ligand being co-ordinated to cobalt as in the ethylenedi-imine system. The appropriate *g* and *A* values are given in Table 3. They were deduced by computer-simulation methods[12] using a model in which the largest *g* value lies along the O–O bond. The magnitudes of the rhombic *g* and *A* tensors are very similar to those of the analogous dioxygen adduct of [Co(sal-1,2-pn)], indicating that the $^{-}SO_3$ ring substituents do not markedly influence the Co–O_2 moiety. The Co–O–O angle is also similar to that deduced for the parent molecule.[13]

The original e.s.r. spectrum of the cobalt(II) complex is regained after passing nitrogen through the solution for some time at room temperature, indicating reversibility for the oxygenation process in agreement with the behaviour of other related superoxo-type cobalt species. Attempts to isolate a solid complex from solution failed to yield a pure sample of the 1 : 1 oxygen complex. E.s.r. examination of the solid isolated indicated the presence of the initial cobalt(II) complex as well as the 1 : 1 oxygen species.

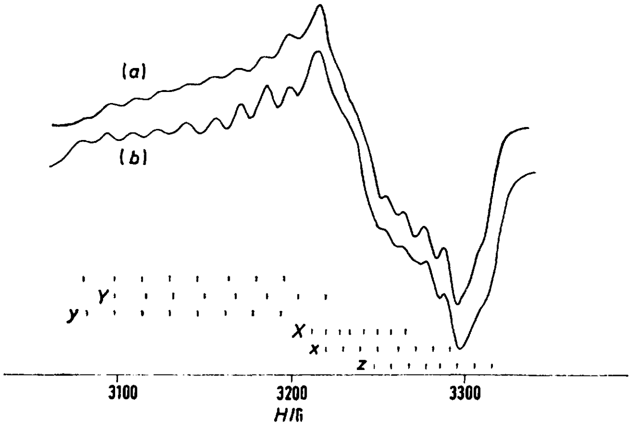


FIGURE 4 E.s.r. spectrum of $[Co(SO_3\text{-sal-1,2-pn})(O_2)]^{2-}$ in frozen dmf–water, 120 K. (*a*) Observed spectrum, (*b*) computer-simulated spectrum (microwave frequency 9 157 MHz)

The *o*-phenylenedi-imine derivative $Na_2[Co(SO_3\text{-salphen})]$ also shows an e.s.r. spectrum in oxygen-free aqueous dmf indicating a tetragonally distorted low-spin d^7 [Co(chelate)L′] complex (Table 2). On addition of oxygen, the cobalt(II) spectrum diminishes markedly in intensity due to the formation of the binuclear peroxo-species $Na_4[\{Co(SO_3\text{-salphen})\}_2(O_2)]$, although a weak spectrum due to a small amount of the superoxo-species can still be detected. This latter complex can be reconverted into the initial cobalt(II) species by the passage of nitrogen at room temperature, but the peroxo-complex is only dissociated when the nitrogen stream is passed through the solution for several hours at 100 °C. The peroxo-complex can be isolated from aqueous dmf solution as in the case of the corresponding SO_3-salen compound.

The complex considered to contain an additional molecule of ethylenediamine co-ordinated to the metal, $Na_2[Co(SO_3\text{-salen})]\cdot NH_2CH_2CH_2NH_2$, shows a well resolved e.s.r. spectrum as the undiluted solid with a ^{14}N triplet structure clearly displayed on the *z* lines in agreement with the co-ordination of one NH_2 group from the ethylenediamine molecule. However, a solution of the complex in aqueous dmf shows an e.s.r. spectrum which no longer provides evidence for ^{14}N hyperfine coupling and is essentially similar to that given by the parent complex $Na_2[Co(SO_3\text{-salen})]$, *i.e.* there is no longer e.s.r. evidence for co-ordination of the ethylenediamine molecule to Co. The addition of more ethylenediamine to this solution still with strict exclusion of oxygen causes rapid loss of the initial e.s.r. signal and this is interpreted as due to the formation of high-spin cobalt(II) species, possibly involving the formation and co-ordination of the tridentate ligands referred to previously. It was observed that when 1,3-propylenediamine was added to a solution of $Na_2[Co(SO_3\text{-salen})]$ the initial e.s.r. spectrum of the complex altered to give ^{14}N hyperfine interactions indicating that some initial co-ordination of the amine had occurred. However, after standing under a nitrogen atmosphere for several hours the solution no longer gave an e.s.r. signal, indicating the formation of high-spin cobalt(II) species although they were clearly formed at a slower rate than when ethylenediamine was involved.

Admittance of oxygen to the solution of $Na_2[Co(SO_3\text{-salen})]\cdot NH_2CH_2CH_2NH_2$ causes the cobalt(II) lines to disappear and no lines due to a superoxo-species are observed. Heating the solution to 100 °C does regenerate the cobalt(II) signal which has an intensity of *ca.* 20% of the original. The results are compatible with reversible formation of a peroxo-bridged complex.

The high-spin complex $Na_2[Co(SO_3\text{-sal-1,3-pn})]$ does not react with oxygen in aqueous dmf solution.

Table 4 demonstrates in a qualitative manner the greater ease of reaction with oxygen of several sulphonated cobalt(II) salicylaldimine compounds compared to their unsulphonated counterparts using aqueous dmf as solvent. An important feature to be noted in both the systems, and which is often overlooked, is the existence of equilibria between 1 : 1 and 2 : 1 dioxygen complexes, the latter being e.s.r. inactive. Recent low-temperature resonance-Raman studies of an isotopically enriched O_2–cobalt Schiff-base complex in aprotic medium clearly shows the co-existence of superoxo- and peroxo-species.[17] The influence of temperature and kinetic factors on the relative proportions of the 1 : 1 and 2 : 1 species has been discussed by Basolo and coworkers.[1]

The Reaction of Oxygen with Solid Complexes.—Earlier studies on the uptake of oxygen by ' active ' forms of [Co(salen)] have indicated the formation of a Co–O_2 2 : 1 complex at room temperature,[18,19] *i.e.* the peroxo-type species are apparently formed even in the absence of any additional Lewis base. The five-co-ordinate salicylaldimine cobalt(II) complex derived from 4-azaheptane-1,7-diylbis(salicylaldimine) has been reported to form a Co–O_2 1 : 1 compound in the solid state,[19] although evidence for the 2 : 1 complex has been presented by Floriani and Calderazzo [14] from studies in various solvents.

The e.s.r. spectrum of solid $Na_2[Co(SO_3\text{-salen})]$, at 120 K, under a nitrogen atmosphere and undiluted with a diamagnetic material, displays a broad signal. On exposure of the solid to oxygen an absorption appears at

TABLE 4

Comparison of the oxygenation of quadridentate cobalt(II) salicylaldiminesulphonate and salicylaldimine compounds *

Complex	Reactions with O_2		Reversibility in solution
	dmf–water	dmf	
$Na_2[Co(SO_3\text{-salen})]$	Rapid at r.t., mainly peroxo-complex; small amount of superoxo-complex detected by e.s.r.		Not readily at r.t., completely at 100 °C over several hours in stream of N_2
[Co(salen)]		(1) Slow reaction at r.t. giving precipitate of peroxo-complex. No superoxo-species detected by e.s.r.	Reversible at 100 °C over several hours in stream of N_2
		(2) Rate not accelerated by addition of water	
		(3) Addition of pyridine caused rapid formation of superoxo-signal but substantial amounts of peroxo-species also formed	Partially reversible at r.t. in stream of N_2, completely at 100 °C in stream of N_2
$Na_2[Co(SO_3\text{-salphen})]$	Rapid at r.t., mainly peroxo-species; small amount of superoxo-species		Reversible at 100 °C over several hours in stream of N_2
[Co(salphen)]		(1) No reaction at r.t.	
		(2) Superoxo-species detected in presence of 15% water	Reversible at r.t.
		(3) Addition of pyridine allows formation of mixture of superoxo- and peroxo-species	Partially reversible at r.t. in N_2 stream, fully reversible at 100 °C

* r.t. = Room temperature.

ca. $g = 2$, characteristic of a superoxo type Co–O_2 complex. The broad features of the original spectrum still remain, although diminished in intensity, suggesting that the complex has been only partially oxygenated. The ' superoxo '-signal is generally not well resolved although some samples examined did show an eight line hyperfine structure on the low-field side of the signal with a small value for A_{Co} of *ca.* 15 G. Heating the oxygenated solid under vacuum at 120 °C led to the complete disappearance of the ' superoxo '-signal leaving only the broad initial absorption of the sample, thus showing that the process is fully reversible under such conditions.

Mukherjee and Rây[4] first reported the synthesis of $Na_2[Co(SO_3\text{-salen})]$ and claimed that the compound did not undergo reaction with oxygen. The magnetic moment reported for their sample was 1.55 B.M. at 30 °C. It appears certain that their preparation contained some proportion of bound oxygen since they did not appear to take any precautions to exclude air from their experiments. The room-temperature magnetic moment of the complex carefully prepared under anaerobic conditions in this work was 2.81 B.M.

It is of interest that the sulphonated [Co(salen)] complex favours the formation of a 1 : 1 ' superoxo '-compound at room temperature whereas the parent complex, in those crystal forms described as ' oxygen active ', reputedly only forms the 2 : 1 ' peroxo '-derivative.[1,19,20] However, as we shall describe in a future communication, e.s.r. studies on oxygenated samples of active [Co(salen)], prepared according to a recent procedure,[20] also show the presence of considerable quantities of O_2–[Co(salen)] in the solid state. Clearly, therefore, the presence of a sulphonate substituent or of a co-ordinated water molecule cannot be the only reasons for activity towards O_2 binding and it is more likely a feature of the crystal-lattice framework.

If the oxygenated sulphonate complex is dissolved in aqueous dmf and a rapid stream of nitrogen passed through the solution, most of the co-ordinated oxygen is released and the e.s.r. spectrum of the complex (at 120 K) returns to that of the original oxygen-free cobalt(II) compound indicating ready reversibility for reaction (1).

$$[Co(SO_3\text{-salen})]^{2-} + O_2 \rightleftharpoons [Co(SO_3\text{-salen})(O_2)]^{2-} \quad (1)$$

The passage of further oxygen through the solution rapidly forms the binuclear peroxo-complex as already described.

The $[Co(SO_3\text{-salen})]$ complex containing another molecule of ethylenediamine shows a remarkable avidity for oxygen. Indeed it has only been found possible to prepare pure samples of the complex by working under rigorously oxygen-free conditions. A pure sample exposed to oxygen rapidly absorbs the gas and gives an extremely well resolved e.s.r. spectrum typical of a superoxo-type cobalt(III) complex. All eight hyperfine lines are clearly defined in the low-field (g_y) region (Figure 5, Table 3). The e.s.r. parameters are similar to those of $[Co(SO_3\text{-sal-1,2-pn})(O_2)]^{2-}$ although there are small differences in detail. The magnetic moment of the pure starting complex is 2.57 B.M. at room temperature and decreases to 2.02 B.M. on formation of the 1 : 1 dioxygen complex. There is no evidence in the final e.s.r. spectrum for the broad absorption of the initial complex, thus indicating virtually total conversion. The co-ordinated oxygen is readily removed by dissolving the sample in aqueous dmf and passing nitrogen through the solution.

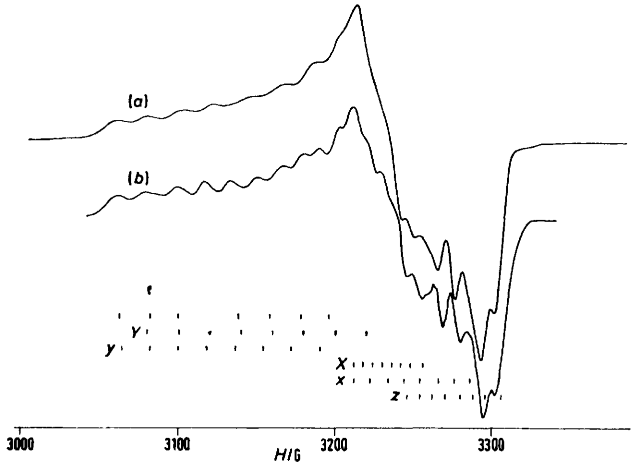


FIGURE 5 E.s.r. spectrum of powdered $[Co(SO_3\text{-salen})(O_2)(en)]^{2-}$ at 120 K. (*a*) Observed spectrum, (*b*) computer-simulated spectrum (microwave frequency 9 147 MHz)

Heating the solid superoxo-complex under vacuum at 115 °C for 6 h causes little change in the e.s.r. spectrum indicating the considerable increase in thermal stability of the complex over the $[Co(SO_3\text{-salen})]$ derivative (Figure 6). At 135 °C however some significant changes occur in the appearance of the spectrum. The broad spectrum characteristic of the cobalt(II) complex in the solid state reappears while the line due to the $Co-O_2$ ' superoxo '-type compound appears greatly reduced in intensity. A narrow ' free-radical ' type resonance line also appears superimposed at 3 200 G. This complicated spectrum is retained by the sample with only minor changes even when it is further heated to 195 °C, although some loss in intensity is observed. When oxygen is readmitted to this heated sample a strong ' superoxo '-signal reappears although it shows much poorer resolution than that of the original sample. It is believed that some loss of ethylenediamine may occur during this period of prolonged vigorous heating.

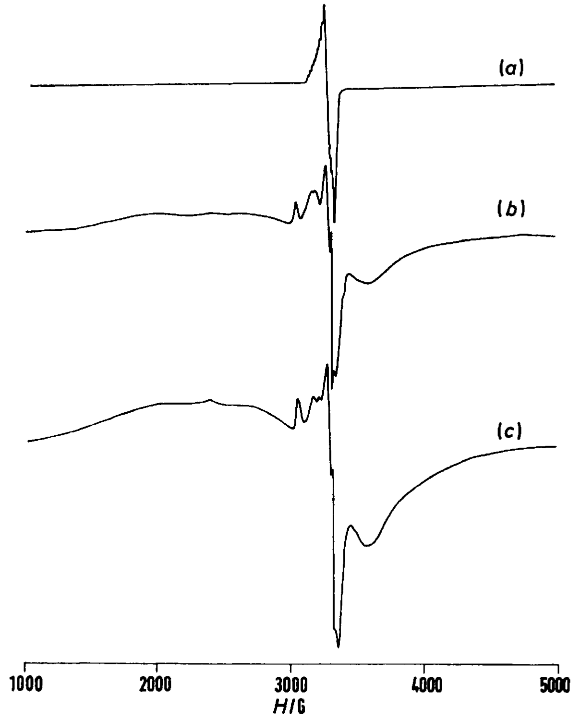


FIGURE 6 Effect on the e.s.r. spectrum of $[Co(SO_3\text{-salen})(O_2)(en)]^{2-}$ of heating *in vacuo* at 23 (*a*), 135 (4 h) (*b*), and 160 °C (4 h) (*c*)

There was little evidence for oxygen absorption in the solid state by the 1,2-propylene or *o*-phenylene sulphonated salicylaldimine complexes. Both solid compounds showed broad isotropic e.s.r. signals similar to that of the $[Co(SO_3\text{-salen})]$ derivative. In the presence of oxygen the 1,2-propylene derivative showed evidence for a very weak and poorly resolved signal at $g \approx 2$ indicating some slight degree of reaction. The *o*-phenylene derivative however showed no evidence for any change in the broad isotropic e.s.r. signal centred at 2 800 G ($g \approx 2.33$). Since both complexes react with oxygen in aqueous solution, failure to react in the solid state may be related to the nature of the solids prepared in this work. As discussed above for [Co(salen)], there may be other crystalline modifications of these complexes which are active towards oxygen in the solid state. Various samples of the complexes prepared under slightly different conditions were examined however without any sign of enhanced oxygen reactivity in the solid state. We note finally that cobalt(II) ' picket-fence ' porphyrins [21] and carboranylporphyrins [22] bind oxygen in the solid state. The published e.s.r. spectra of the 1 : 1 species generally display much inferior resolution to those obtained here.

EXPERIMENTAL

E.s.r. spectra were obtained at *X*-band frequency using a Varian E12 instrument. Infrared spectra were recorded on a Jasco IRA 1 spectrometer. Magnetic moments were determined using the Faraday method.

Salicylaldehyde-5-sulphonic Acid, the Disodium Monohydrate Salt.—The method of preparation was adapted from Blau.[23]

N-Phenylsalicylaldimine (35 g) was added to concentrated sulphuric acid (95 cm³) and the mixture heated for 2 h with occasional stirring, keeping the temperature in the range 100 ± 5 °C. After cooling, the solution was slowly added to ice–water (1 l) with vigorous stirring to precipitate the yellow product. The mixture was reheated until all the solid had redissolved then allowed to cool. The yellow crystalline *N*-phenylsalicylaldimine-5-sulphonic acid was filtered off, washed with small quantities of ice–water, then ethanol and acetone and dried in air. Yield, 25.5 g.

The salicylaldimine-5-sulphonic acid (25.5 g) was dissolved in boiling water (500 cm³) and anhydrous sodium carbonate (8.4 g) added in small quantities. After CO_2 evolution had ceased, aniline was removed by passing a continuous stream of air through the boiling solution for several hours, water being added as necessary to maintain the volume. The solution was finally evaporated to dryness and the residue purified by extraction several times with ethanol followed by dissolution in water and precipitation with ethanol as white crystals (20 g).

$Na_2[Co(SO_3\text{-sal})_2]\cdot 3H_2O$.—The compound $CoCl_2\cdot 6H_2O$ (6 g, 25 mmol) in water (30 cm^3) was added to a solution of disodium salicylaldehyde-5-sulphonate (13.2 g, 50 mmol) in water (20 cm^3) and the mixture heated for 10 min. After filtering the hot solution, it was concentrated and allowed to cool to yield the yellow crystalline complex (12 g).

Cobalt(II) *Complexes with* NN′-*Substituted Bis*(*salicylaldimine-*5-*sulphonates*).—All operations involving these complexes were conducted under an atmosphere of purified nitrogen. In a typical experiment deaerated ethanol (100 cm^3), water (15 cm^3), and ethylenediamine (0.6 g, 10 mmol) were added to $Na_2[Co(SO_3\text{-sal})_2]\cdot 3H_2O$ (5.5 g, 10 mmol) and the mixture refluxed under a nitrogen atmosphere for 1 h. The dark brown feathery precipitate was filtered off under nitrogen and dried by passage of a nitrogen stream at room temperature (5.7 g). Similar procedures were used to prepare derivatives from 1,2- and 1,3-propylenediamines and *o*-phenylenediamine.

The complex containing an additional mol of ethylenediamine was prepared by an identical procedure except that a four-fold excess of the diamine was added at the initial stage and refluxing continued for 4 h.

Microanalytical figures are given in Table 1.

The Peroxo-complexes.—The compound $Na_2[Co(SO_3\text{-salen})]\cdot 2H_2O$ (1 g) was dissolved in water (5 cm^3) and a stream of air passed through the solution for 20 min. Ethanol was carefully added to the green-brown solution until a precipitate commenced to form. The solution was filtered and the filtrate placed in a desiccator in an atmosphere of ethanol vapour. Green-brown crystals of $Na_4[\{Co(SO_3\text{-salen})\}_2(O_2)]\cdot 10H_2O$ slowly deposited. Compounds derived from the 1,2-propylene and *o*-phenylenediamine cobalt complexes were similarly prepared.

Recrystallisation of the ethylenedi-imine–oxygen complex from 1 : 1 water–t-butyl alcohol containing excess of NH_3 or imidazole gave brown crystalline products which analysed as the species $Na_4[\{Co(SO_2\text{-salen})L'\}_2(O_2)]\cdot xH_2O$.

Organometallic Complexes.—In a typical experiment $Na_2[Co(SO_3\text{-salen})]\cdot 2H_2O$ (1 g) was slurried with ethanol (80 cm^3) under nitrogen, and a solution of sodium tetrahydroborate (0.3 g) and sodium hydroxide (3 g) in water (20 cm^3) was added. After 1 min, three drops of an aqueous solution of $K_2[PdCl_4]$ (0.07 mol dm^{-3}) in dilute HCl were added and the mixture rapidly changed from brown to green. When gas evolution had ceased, excess of methyl iodide (1 cm^3) was added and the mixture rapidly turned red-brown. The methylcobalt(III) complex was isolated as well formed red-brown crystals. The other organometallic complexes were prepared in a similar manner. The analytical figures are given in Table 1.

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