Syntheses of *NN'*-Ethylenebis(salicylideneiminate) Transition-metal Chelates by Oxidative Decarbonylation

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Reaction of *NN'*-ethylenebis(salicylideneiminato)mercury(II), [Hg(salen)], with certain transition-metal carbonyls leads to the formation of the corresponding chelate of the transition-metal ion with deposition of mercury or the formation of mixed-metal chelates. Thus $[Cr(CO)_6]$ and $[Mo(CO)_6]$ give $[Cr(salen)]_2O$ and $[MoO(salen)]_2O$ respectively. The compound $[\{Fe(cp)(CO)_2\}_2]$ (cp = η-cyclopentadienyl) gives Hg(salen)·Fe(cp)(salen) which on treatment with glacial acetic acid yields $[Fe(salen)]O_2CMe$. Dicobalt octacarbonyl gives $Hg(salen)\cdot Co(CO)_3$ which when heated in pyridine or dimethylformamide yields [Co(salen)] with deposition of mercury.

TRANSITION-METAL-ION carbonyl compounds have been used in the preparation of a wide range of complexes which result from the replacement of carbonyl groups by neutral ligands.[1-5] In addition, investigations into the use of metal carbonyl compounds in the preparation of chelate compounds by oxidative decarbonylation have been carried out, particularly for transition-metal-ion chelates of carboxylates,[6-16] β-keto-enolates,[17-23] thio-ligands,[24-36] quadridentate Schiff bases,[37-39] and porphyrins.[40-49]

Recent investigations into the Lewis-base properties of transition-metal-ion Schiff-base complexes have shown that [M(salen)] complexes [M = Co, Ni, or Cu; salen = *NN'*-ethylenebis(salicylideneiminate)] react with the halides SnX_4 and SnX_2 (where X = Cl or Br) to form 1 : 1 adducts.[50] To further clarify the question of the local symmetry about the acceptor metal in such adducts, substitution products of the form $[Ni(salen)M'(CO)_4]$ (where M' = Mo or W), $[Ni(salen)M'(CO)_3X]$ (where M' = Mn or Re, X = Cl or Br), and $[Ni(aben)Mn(CO)X_3]$ [aben = *NN'*-ethylenebis(*o*-aminobenzylideneiminate), and X = Cl or Br] were isolated. The i.r. spectra of these compounds, particularly over the carbonyl region, were used to assign structures.[51] Although metal-exchange processes were not found to occur for these systems, it did raise the possibility that, under suitable conditions, unusual Schiff-base complexes could be prepared if a system were found which made exchange reactions possible. It has now been shown that reaction of the mercury(II) Schiff base, [Hg(salen)], with certain transition-metal carbonyls, in general, leads to the deposition of metallic mercury and the production of transition-metal Schiff-base complexes.

RESULTS AND DISCUSSION

Properties of the Mercury(II) *Chelate Compounds.*—The preparation of mercury(II) Schiff bases has previously been described.[52] In general, the Schiff-base complexes are yellow, extremely insoluble, microcrystalline powders. Unfortunately, no structural determination has been reported for [Hg(salen)], although tetrahedral stereochemistry about the metal ion and polymeric aggregation has been proposed.[52]

In order to monitor the course of the reaction of mercury(II) chelates with the transition-metal-ion carbonyls, the e.s.r. spectra of freshly prepared mercury chelates were studied. The mercury chelates are diamagnetic and it was not expected that they would give rise to e.s.r. signals but surprisingly a single resonance at $g = 2.0023$ could be detected at high instrument gains. Several other mercury(II) Schiff bases, based on the general salen type, were subsequently prepared and their e.s.r. spectra collected. Although it is emphasized that in all cases the signal is very weak, comparison of peak heights leads to the following decreasing order of intensity: *NN'*-ethylenebis(naphthylideneiminate), napen > *NN'*-ethylenebis(α-methylsalicylideneiminate),α,α'-Me_2salen ≫ *NN'*-ethylenebis(3-methoxysalicylideneiminate),3,3'-$(MeO)_2$salen > *NN'*-ethylenebis(salicylideneiminate), salen ≫ *NN'*-ethylenebis(benzoylacetoneiminate), bzacen. It is worth noting that this signal is not present in the free ligands and is observed only after chelation of the mercury ions.

It is believed that these signals may be attributed to the presence of a free radical in the mercury chelates, for the following reasons. First, the signal is isotropic and is centred on $g = 2.0023$ as expected for free radicals. Secondly, the presence of similar narrow isotropic lines centred on $g \approx 2$, observed in the e.s.r. spectra of crystals and polycrystalline powders of other diamagnetic macrocyclic complexes, such as those of phthalocyanines and porphyrins, have also been attributed to free-radical species.[53] Whilst the origin of these lines in the phthalocyanines is still controversial,[54] it is believed that they arise out of either decomposition products or the presence of molecular oxygen trapped on the surface and in the bulk of the crystalline samples. In the present context another possibility is the presence of small amounts of monomeric mercury(I) species. These ions have recently been observed as transient radical species in pulse-radiolysis studies of the reduction of mercury(II) salts by hydrated electrons.[55] Because of the insolubility of these mercury Schiff bases in organic solvents, a recrystallization process could not be used to ascertain whether the relative intensity of these signals could be reduced.

Reactions of [Hg(salen)] *with Transition-metal-ion Carbonyls.*—(*a*) *Chromium hexacarbonyl.* The reaction of [Hg(salen)] with chromium hexacarbonyl in refluxing toluene leads to the production of an insoluble light brown microcrystalline powder. A minor product could also be obtained on reduction of the volume of the filtrate. Based on the amount of metallic mercury deposited, an overall conversion, from mercury(II) chelate into chromium(III) chelate, of 90% was calculated. An elemental analysis of the major product was consistent with the empirical formula $[Cr(salen)]_2O$. An i.r. spectrum showed characteristic Schiff-base absorptions at 1 627 and 1 540 [ν(C=N)], 1 469 (deformation of the ethylene bridge), 1 198 (*ortho*-substituted phenyl-ring vibrations), and two bands in the region 725—760 cm^{-1} (aromatic C–H bending vibrations). The appearance of bands at 854 and 870 cm^{-1} in the i.r. spectrum of $[(NH_3)_5CrOCr(NH_3)_5]Br_4$ has been used previously to suggest the presence of the Cr–O–Cr moiety.[56] Similar bands have been observed for the complex at 858 and 870 cm^{-1}, although it is possible that the first of these bands is accidentally degenerate with one of the ligand modes.

Measurement of the magnetic moment, by the Gouy method, yielded $\mu_{eff.} = 2.2$ B.M.* per chromium atom. On theoretical grounds, Dunitz and Orgel [57] concluded that in the binuclear oxo-bridged ruthenium complex $K_4[Cl_5Ru–O–RuCl_5]\cdot H_2O$ the observed diamagnetism and linear Ru–O–Ru unit could be explained in terms of the concept that π bonds are formed between the ruthenium and oxygen atoms. They described the bonding situation as ' resonance between a number of structures, the extremes of which are $(Cl_5Ru^{IV}–O^{2-}–Ru^{IV}Cl_5)$ and $(Cl_5Ru^{II}=O^{2+}=Ru^{II}Cl_5)$.' On the other hand, Figgis and Lewis [58] suggested that for hydroxy-bridged complexes, Cr–OH–Cr, a bridging angle of 120° would be expected. Crystal-structure determinations [59] of the basic rhodo and the acid erythro compounds show that in the oxo-bridged dimer there is a linear Cr–O–Cr moiety, an eclipsed configuration of the two penta-amine units, and a rather short Cr–O bond distance of 1.82 Å. The Cr–Cr distance is 3.64 Å. In the hydroxy-bridged salt there is a bent Cr–O–Cr linkage with an angle of 168 ± 5° and Cr–Cr distance of 3.91 Å. At room temperature, typical hydroxy-bridged chromium complexes are found to exhibit magnetic moments in the range 2.3—4.0 B.M. whereas oxo-bridged systems range from diamagnetic to 2.3 B.M.

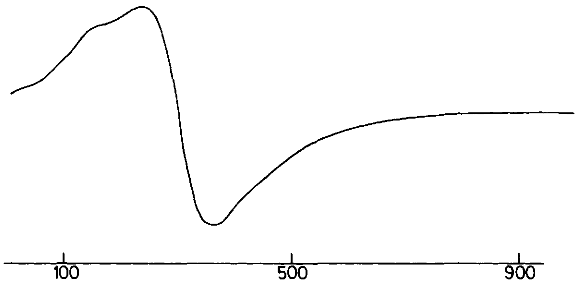

FIGURE 1 E.s.r. spectrum of $[Cr(salen)]_2O$ at −140 °C; microwave frequency 9.147 GHz

The e.s.r. spectrum of the insoluble microcrystalline powder at −140 °C shown in Figure 1 confirms that the chromium is trivalent.

On the basis of these observations, an oxo-bridged chromium(III) complex is proposed. The exact nature of the bridging unit between the two chromium atoms must await an *X*-ray crystal-structure determination, although it is possible that the complex may be similar to the oxo-bridged iron(III) salen complex, $[\{Fe(salen)\}_2O]$.[60,61]

The reaction of [Hg(salen)] with $[Cr(CO)_6]$ was also shown to produce a small amount of a more soluble light brown product. The i.r. spectrum of a freshly prepared sample showed carbonyl bands in the 1 850—2 000 cm^{-1} region. However, on standing, it was observed that the complex was unstable with respect to these bands. An elemental analysis of the resulting product was identical to that obtained for the oxo-bridged complex described previously. Possibly this carbonylated product may be an intermediate in the reaction sequence which eventually leads to $[Cr(salen)]_2O$.

Reaction of $[Cr(CO)_6]$ with the free ligand, H_2salen, under similar conditions to the corresponding mercury chelate reaction leads to the formation of another light brown insoluble microcrystalline powder. An elemental analysis of this material is close to that obtained by Mabbs and co-workers [62] for a complex formulated as $[Cr(salen)(OH)]\cdot 0.5H_2O$. An i.r. spectrum (Nujol mull 4 000—625 cm^{-1}) shows the characteristic Schiff-base peaks as well as a broad band at 3 200—3 450 cm^{-1}. The appearance of this band gives support for a degree of hydration. The room-temperature magnetic moment was observed to be 3.43 B.M. which is identical to that obtained previously. No detailed interpretation of the observed magnetic properties at reduced temperatures was given for this complex due to the variability between samples obtained from different preparations and the inability to determine its molecularity. Magnetic moments for a variety of other chromium(III) salen derivatives generally possess values in the range 3.86—3.95 B.M.[62]

(*b*) *Molybdenum hexacarbonyl.* Refluxing a suspension of [Hg(salen)] with molybdenum hexacarbonyl for 2 h in toluene leads to the production of a dark brown microcrystalline powder. An elemental analysis of this product corresponds to the empirical formula $[MoO(salen)]_2O\cdot 1.5C_6H_5Me$. Heating the sample under reduced pressure brings about a weight loss which is associated with the loss of the toluene. An i.r. spectrum showed bands at 1 601, 1 540, 1 153, 1 123, and 762 cm^{-1}, characteristic of transition-metal salen derivatives. Two strong bands are also found at 903 and 930 cm^{-1}, and also a strong peak at 762 cm^{-1}.

The assignment of the Mo–O stretching frequencies of

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* Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2.

oxomolybdenum complexes, especially when other ligands of some complexity are present, has previously been shown to be difficult. One approach [63] has been to examine the molybdenum–oxygen frequencies of $[NEt_4]_4[Mo_2O_3Cl_8]$. With the absence of organic ligands the assignment of its i.r. spectrum is particularly simple; two bands at 983 and 958 cm^{-1} were postulated as arising from molybdenum–oxygen (terminal) stretching frequencies whilst a band at 735 cm^{-1} was attributed to one of the bridging antisymmetric or symmetric stretching frequencies.

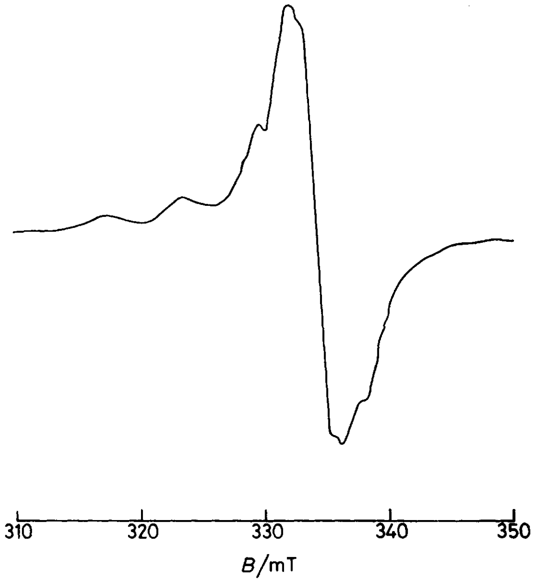

FIGURE 2 E.s.r. spectrum of a pyridine solution of $[MoO(salen)]_2O$ (1.0×10^{-3} mol dm^{-3}) at −140 °C; microwave frequency 9.147 GHz

With this in mind, the peaks at 903 and 930 cm^{-1} of the present complex are tentatively assigned to the Mo–O stretching frequencies, whilst that at 762 cm^{-1} is assigned to the bridging molybdenum–oxygen frequency.

The magnetic moment per molybdenum atom at room temperature was 0.98 B.M. The complex is therefore paramagnetic with a reduced magnetic moment possibly due to exchange coupling. The e.s.r. spectrum of a frozen solution of the complex in pyridine shown in Figure 2 confirmed that the complex was paramagnetic.

A preliminary account has recently been published [38] of the reaction of H_2salen with $[Mo(CO)_6]$ in dimethylformamide solution and between the molten reactants. The analytical data and diamagnetism of the purple oxomolybdenum species obtained in both cases could not distinguish between the two possible structures involving molybdenum(IV), [MoO(salen)], or molybdenum(V), $[MoO(salen)]_2O$. Another report [39] showed that if the reaction was performed in toluene solution then Schiff bases were not produced. Instead, hydrogenation of the ligand occurred giving rise to dicarbonyl-[*NN'*-ethylenebis(salicylaminato)]molybdenum(II). This complex shows a distinct N–H vibration at 3 265 cm^{-1}, but the ν(C=N) band expected at *ca.* 1 550 cm^{-1} is absent.

In the reaction involving [Hg(salen)], no sharp stretching vibrations were observed in the 3 200—3 300 cm^{-1} region and the ν(C=N) bands assigned at 1 595 and 1 540 cm^{-1} were obviously present indicating that hydrogenation had not taken place.

A report has also been made on the preparation of a dioxomolybdenum(VI) salen derivative.[64] The yellow crystals were obtained by refluxing bis(acetylacetonato)-dioxomolybdenum(VI) in methanol with the Schiff-base ligand. On the basis of i.r. and ^1H n.m.r. spectra it was concluded that the MoO_2 group possessed a *cis* structure.

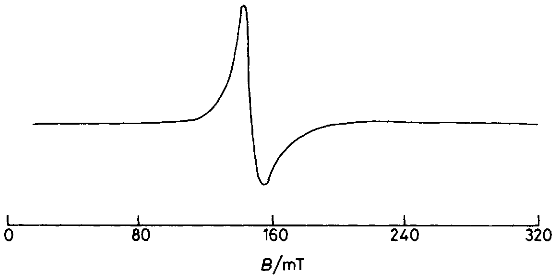

FIGURE 3 E.s.r. spectrum due to a chloroform solution of $[Fe(salen)]O_2CMe$ (1.0×10^{-3} mol dm^{-3}) at −140 °C; microwave frequency 9.147 GHz

(*c*) *η-Cyclopentadienyliron dicarbonyl dimer.* Oxidative decarbonylation reactions involving the iron carbonyl derivative $[\{Fe(cp)(CO)_2\}_2]$ (cp = cyclopentadienyl) have previously been shown [30,31] to result in retention of the cyclopentadienyl group. It was therefore of interest to see whether the previously unknown η-cyclopentadienyliron(III) salen complex could be prepared by the reaction of the iron carbonyl derivative with [Hg(salen)].

When a suspension of [Hg(salen)] is refluxed under toluene with a freshly recrystallized sample of $[\{Fe(cp)(CO)_2\}_2]$ for 2 h a light brown insoluble microcrystalline powder is produced as an intermediate. Further reaction of this material may lead to the known iron(III) salen derivatives $[Fe(salen)]O_2CMe$ or $[\{Fe(salen)_2\}_2O]$ in high yields. If the sample of the intermediate is suspended in ethyl acetate and a small amount of glacial acetic acid added a brilliant red solution develops and metallic mercury is deposited. Reduction of the volume of the red solution yielded a crimson crystalline solid, which, on the basis of analytical data, i.r. and e.s.r. spectra (Figure 3), compared with an authentic sample in frozen toluene solution, was shown to be $[Fe(salen)]O_2CMe$. If the complex is suspended in refluxing pyridine, however, metallic mercury is again deposited and an orange powder can be isolated. Comparison of the i.r. spectrum with an authentic sample of $[\{Fe(salen)\}_2O]$ showed the two complexes to be identical.

An elemental analysis of the mixed-metal intermediate chelate pointed to an empirical formula Hg(salen)·Fe(cp)-(salen). An e.s.r. spectrum of the microcrystalline powder at −140 °C showed the presence of high-spin iron(III) ions. This was confirmed by a room-temperature magnetic moment, $\mu_{eff.} = 5.80$ B.M. The i.r. spectrum showed characteristic Schiff-base bands while a more detailed comparison of the i.r. spectra of $[\{Fe(cp)(CO)_2\}_2]$, ferrocene $[Fe(cp)_2]$, [Hg(salen)], and $[Fe(salen)]O_2CMe$ showed that the bands in the 830 cm^{-1} region could safely be assigned to the cyclopentadienyl anion.

The preparation of [Fe(salen)R} (R = Ph or CH_2Ph) have previously been reported.[65,66] Magnetic susceptibility measurements have shown that the compounds are high spin.

(*d*) *Dicobalt octacarbonyl.* An elemental analysis of the orange-brown insoluble microcrystalline powder, obtained by reaction of a freshly filtered heptane solution of dicobalt octacarbonyl with a suspension of [Hg(salen)] in heptane at 50 °C under anaerobic conditions, yielded the empirical formula $Hg(salen)\cdot Co(CO)_3$. Microscopic examination of samples taken from the reaction mixture, at 15-min intervals, clearly showed that after 1.5 h the sample was homogeneous. At shorter reaction times two crystalline forms could readily be perceived. The i.r. spectrum of the complex showed several bands in the terminal carbonyl group region (1 950—2 100 cm^{-1}) confirming their presence, and characteristic Schiff-base absorptions were also apparent. Refluxing a sample of the complex in pyridine or dimethylformamide leads to the deposition of metallic mercury and formation of [Co(salen)], which, in the presence of molecular oxygen, readily undergoes oxygenation.

The intermediate complex was found to be unstable and on standing lost all carbonyl groups, as determined by the i.r. spectrum. Carbonyl groups were also lost from one of the chromium(III) products, as discussed previously.

Magnetic measurements of the intermediate showed that the complex possessed magnetic field dependent properties. However, no change in susceptibility was encountered with the subsequent decomposition of the intermediate and so it is assumed that traces of metallic cobalt were present as impurities in the sample, since metallic cobalt is known to be ferromagnetic.

Calderazzo *et al.*[37] have reported that the reaction of H_2salen with $[Co(CO)_8]$ in dimethylformamide (dmf) yields the cobalt(II) Schiff base in 42.5% yield. However, dimethylformamide is known to react with $[Co_2(CO)_8]$ according to the reaction (1) so that perhaps

$$3[Co_2(CO)_8] + 12Me_2NCHO \longrightarrow 2[Co^{II}(dmf)_6][Co(CO)_4]_2 + 8CO \quad (1)$$

this should not be viewed as a typical oxidative decarbonylation reaction.

When $[Co_2(CO)_8]$ was heated at 50 °C (below its decomposition temperature of 51—52 °C) in heptane with *NN'*-ethylenebis(acetylacetoneimine), for 4 h, a product formulated as $[Co(Schiff\ base)_3][Co(CO)_4]_2$ was obtained.[37] The tetracarbonylcobaltate was found to be sensitive to air in the solid state. The i.r. spectrum showed the carbonyl-stretching vibration characteristic of the $[Co(CO)_4]^-$ anion at 1 885 cm^{-1}.

EXPERIMENTAL

E.s.r. spectra, recorded as the first derivative of the absorption signal, were measured on a Varian E-12 spectrometer. Measurements were carried out at sample temperatures between 20 and −140 °C. Low-temperature measurements were made in a solution cell consisting of narrow-bore silica tubing. A Varian E246 flat quartz cell, designed to minimize dielectric loss, was employed for *X*-band measurements on solutions.

Microanalyses were carried out by the Australian Microanalytical Service, the results being shown in the Table.

Analytical data (%) for M(salen) derivatives

	Found			Required		
Complex	C	H	N	C	H	N
$[Cr(salen)]_2O$	58.9	4.70	8.30	58.9	4.30	8.60
$[Cr(salen)(OH)]\cdot H_2O$	54.8	4.60	7.90	54.4	4.80	7.90
$[MoO(salen)]_2O\cdot 1.5C_6H_5CH_3$	55.9	4.45	6.00	56.05	4.45	6.15
Hg(salen)·Fe(cp)(salen)	52.05	4.20	6.70	52.05	3.90	6.55
$Hg(salen)\cdot Co(CO)_3$	37.4	2.40	4.55	37.4	2.30	4.60

The magnetic susceptibilities were determined by means of a Gouy balance. Infrared spectra of compounds as Nujol mulls were recorded with a Perkin-Elmer 257 (4 000—625 cm^{-1}) spectrophotometer and calibrated with polystyrene film. All compounds were examined under a microscope to test for homogeneity and crystal habit.

The source of mercury(II) was analytical grade mercury(II) acetate obtained from Koch-Light. Salicylaldehyde was obtained from B.D.H., ethylenediamine and sodium diethyldithiocarbamate from May and Baker, and the transition-metal carbonyl compounds from Alfa Inorganics.

Preparation of N,N'-*Ethylenebis*(*salicylideneiminato*)-*mercury*(II).—Mercury(II) acetate (15.94 g) was dissolved in boiling ethanol, containing a few drops of distilled water. The clear colourless filtered solution was then added to a refluxing ethanolic solution of H_2salen (13.42 g). The resulting bright yellow precipitate was washed with boiling absolute ethanol (3 × 50 cm^3) and air dried (Found: C, 40.9; H, 3.2; N, 6.2. Calc. for $C_{16}H_{14}HgN_2O_2$: C, 41.15; H, 3.00; N, 6.00%), yield = 90%. The compound was insoluble in all common solvents except glacial acetic acid from which it could not be recovered.

The other mercury(II) Schiff bases, derived from the ligands napen, α,α'-Me_2salen, 3,3'-$(MeO)_2$salen, and bzacen were prepared in a similar manner and were all obtained as insoluble yellow microcrystalline powders.

Reaction of NN'-*Ethylenebis*(*salicylideneiminato*)*mercury*(II) *with Chromium Hexacarbonyl.*—Chromium hexacarbonyl (1.0 g) was dissolved in sodium-dried toluene, heated to reflux under anaerobic conditions, and [Hg(salen)] (2.33 g) added as a suspension in toluene (30 cm^3). After several hours the colour began to deepen from yellow to brown and the mixture was left to reflux for a total of 10 h under a nitrogen atmosphere. Any sublimed $[Cr(CO)_6]$ was washed back down the condenser into the reaction flask. The metallic mercury deposited at the bottom of the flask was collected and accounted for a 90% recovery. The remaining mixture was filtered hot to obtain two products: product (1), an insoluble light brown microcrystalline powder; (2), a slightly soluble (toluene) light brown microcrystalline powder (obtained from the filtrate). Infrared spectra of these products showed that, apart from two bands in the terminal carbonyl group region, they were very similar. Product (2) was found to be unstable with respect to the carbonyl groups and loss of carbon monoxide led to product (1). The room-temperature magnetic moment of (1) (Gouy method) was $\mu_{eff.} = 2.2$ B.M. The e.s.r. spectrum of the microcrystalline product (1) at −140 °C confirmed that the complex was paramagnetic.

No difference in the product could be detected whether the reaction was performed either in the presence or absence of air.

Reaction of NN′-*Ethylenebis*(*salicylideneimine*) *with Chromium Hexacarbonyl.*—Similar reaction conditions as for the previous experiment were employed: $[Cr(CO)_6]$ (2.2 g) and H_2salen (2.7 g). After refluxing for 8 h under a nitrogen atmosphere the mixture was filtered and the product washed with several volumes of boiling toluene (yield 2.96 g, 85%). The i.r. spectrum (Nujol mull, 4 000—625 cm^{-1}) and the magnetic moment ($\mu_{eff.} = 3.43$ B.M.) were recorded. A small broad i.r. band in the region 3 200—3 450 cm^{-1} was attributed to the presence of moisture. The analytical data and the magnetic moment obtained for this complex suggested that it was the same as a compound isolated by Mabbs and co-workers[62] and formulated as $[Cr(salen)(OH)]\cdot 0.5H_2O$. Analytical data are given in the Table.

Reaction of NN′-*Ethylenebis*(*salicylideneiminato*)*mercury*(II) *with Molybdenum Hexacarbonyl.*—Molybdenum hexacarbonyl (0.53 g) and [Hg(salen)] (0.93 g) were refluxed under a nitrogen atmosphere in sodium-dried toluene for 2 h. The hot reaction mixture was decanted from the metallic mercury deposited (65% Hg recovery) and filtered hot. A brown microcrystalline powder was obtained (yield 0.26 g) (Table). The i.r. spectrum (Nujol mull, 4 000—625 cm^{-1}) was collected and the magnetic moment measured (0.98 B.M.). An e.s.r. spectrum of the complex in a frozen pyridine solution was recorded at −140 °C and confirmed that the complex was paramagnetic.

Reaction of NN′-*Ethylenebis*(*salicylideneiminato*)*mercury*(II) *with* η-*Cyclopentadienyliron Dicarbonyl Dimer.*—The compound [Hg(salen)] (2.33 g) was suspended in refluxing dry toluene and a solution of a freshly recrystallized sample (ethyl acetate) of $[\{Fe(cp)(CO)_2\}_2]$ (0.89 g) added. The reaction mixture was refluxed for 2 h and the light brown intermediate isolated by filtration. The i.r. spectrum (Nujol mull, 4 000—625 cm^{-1}) showed the absence of any carbonyl group stretching vibrations but clearly showed the characteristic Schiff base absorptions. Comparison with $[\{Fe(cp)(CO)_2\}_2]$, ferrocene $[Fe(cp)_2]$, [Hg(salen)], and $[Fe^{III}(salen)]O_2CMe$ showed the presence of the cyclopentadienyl moiety, giving two bands in the 830 cm^{-1} region. A room-temperature magnetic moment (Gouy method) showed the compound to be paramagnetic ($\mu_{eff.} = 5.80$ B.M.) and was explained in terms of the iron being present in the high-spin iron(III) state. This was confirmed by an e.s.r spectrum of a microcrystalline sample (−140 °C). Microanalysis (C,H,N) gave the values listed in the Table.

Preparation of NN′-*Ethylenebis*(*salicylideneiminato*)-*iron*(III) *Acetate.*—A sample of the light brown intermediate isolated above was suspended in refluxing ethyl acetate (50 cm^3). On addition of glacial acetic acid (2 cm^3) a deep red solution developed and metallic mercury was deposited. After filtering the hot solution a crimson solid was obtained by addition of hexane (20 cm^3). Recrystallization from chloroform afforded small crimson crystals in high yield. An e.s.r. spectrum of a frozen chloroform or ethanol solution was identical to that obtained for an authentic sample (Found: C, 53.1; H, 4.60; N, 6.95. Calc. for $C_{18}H_{18}FeN_2O_4$; C, 52.95; H, 4.55; N, 6.85%).

Preparation of μ-*Oxo-bis*[NN′-*ethylenebis*(*salicylideneiminato*)*iron*(III)].—When a sample of the light brown intermediate was suspended in pyridine and refluxed for 10 min an orange solution developed and metallic mercury was deposited. After filtration and reduction of the volume of the solution an orange solid was obtained. The i.r. spectrum was found to be identical to that obtained from an authentic sample of $[\{Fe(salen)\}_2O]$ (Found: C, 58.3; H, 4.25; N, 8.45. Calc. for $C_{32}H_{28}Fe_2N_4O_5$; C, 58.2; H, 4.25; N, 8.5%).

Reaction of NN′-*Ethylenebis*(*salicylideneiminato*)*mercury*(II) *with Dicobalt Octacarbonyl.*—Dicobalt octacarbonyl (0.86 g) was dissolved in heptane and filtered under a nitrogen atmosphere. A suspension of [Hg(salen)] (2.34 g) was added and the mixture was heated at 50 °C under a constant stream of nitrogen gas. At 15-min intervals a sample was removed for microscopic examination. After 1.5 h only one microcrystalline form could be detected. The shape of this form was similar to that observed for [Hg(salen)]. The orange-brown product was collected by filtration (yield, 3.0 g) and found to be insoluble in all common organic solvents and water. An i.r. spectrum showed the presence of terminal CO bands (1 950—2 100 cm^{-1}) as well as the characteristic Schiff-base peaks.

Preparation of NN′-*Ethylenebis*(*salicylideneiminato*)-*cobalt*(II).—When a sample of the above intermediate was refluxed in pyridine or dimethylformamide under nitrogen, metallic mercury was deposited and a red-brown solution produced. The e.s.r. spectra of this solution, and after reaction with molecular oxygen, were identical to that obtained for an authentic sample of [Co(salen)].

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