

## Preparation and Physico-chemical Properties of Bis(salicylaldehyde hydrazone)-iron(III), manganese(III) and chromium(III) Iodides

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### Abstract

Bis(salicylaldehyde hydrazone)iron(III) iodide has been prepared by reduction of tris(salicylaldehyde hydrazone)iron(III) with hydrazine in dimethylformamide solution followed by reaction with methyl iodide. This reaction has been shown to involve an iron(I) chelate intermediate. Reaction of bis(salicylaldehyde hydrazone)iron(II) with iodine in dimethylformamide solution also leads to formation of bis(salicylaldehyde hydrazone)iron(III) iodide. The reaction of methyl iodide with a dimethylformamide solution of bis(salicylaldehyde hydrazone)manganese(II) and hydrazine leads to the formation of bis(salicylaldehyde hydrazone)-manganese(III) iodide which can also be obtained by reaction of the manganese(II) chelate with iodine. The reduction pathway has been shown to involve the formation of a manganese(0) hydrazine chelate while the use of hydroxylamine, sodium borohydride and sodium dithionite for the reduction of the manganese(II) chelate lead to the formation of a manganese(I) intermediate. Bis(salicylaldehyde hydrazone)chromium(III) nitrate forms as a result of the reaction of hydrated chromium(III) nitrate with salicylaldehyde hydrazone in dimethylformamide and has been used to prepare the corresponding iodide, chloride, bromide, thiocyanate and cyanide by anion exchange reactions in dimethylformamide. Each product has been characterized by the observation of well resolved ESR spectra.

### Introduction

Metal ion coordination circumstances which involve an almost complete occupation of the coordination sphere but leaving one position filled by a solvent molecule or by a replacement anion may prove to be convenient sources of reactive intermediates from which further products may be obtained. Thus, the facile replacement of a solvent

molecule could be the basis of catalytic process while replacement of an anionic group may be used to prepare, for example, new organometallic compounds. The present work describes the preparation of chelates of the type bis(salicylaldehyde hydrazone) M(III) iodide where M = iron, manganese or chromium.

### Experimental

The ESR spectra, recorded as the first derivatives of absorption, were obtained by a Varian E-12 spectrometer with an E-101 microwave bridge at X-band (*ca.* 9.15 GHz). Low temperatures were achieved by means of an E-257 variable temperature accessory (above *ca.* 100 K) or at liquid nitrogen temperature using narrow tail quartz Dewars. Magnetic fields were calibrated against a proton NMR. Microwave frequencies were measured using an EIP 548A frequency counter. Computer simulations were carried out using a VAX computer at the Monash Computer Centre on line to a Servogor digital plotter.

Electronic spectra in the visible region were recorded on a Varian 635 spectrophotometer at room temperature using 1 cm glass and silica cells. Magnetic susceptibility measurements were made by the Gouy method.

The iron(III) and manganese(II) chelates of salicylaldehyde hydrazone were prepared as outlined earlier [1, 3].

#### *Preparation of Bis(salicylaldehyde hydrazone)-iron(III) Iodide Monodimethylformamide*

(a) Under an atmosphere of dinitrogen hydrazine hydrate (5 ml) was mixed to a dmf (50 ml) solution of tris(salicylaldehyde hydrazone)iron(III). An immediate colour change occurred from red–brown to a light chocolate. Methyl iodide (3 ml) was added to the reaction mixture whereupon a brown precipitate separated from solution and was isolated by filtration and washed with hot methanol and pumped free of

solvent at diminished pressure (0.1 mmHg). The yield of bis(salicylaldehyde hydrazone)iron(III) iodide monodimethylformamide was 4.8 g, 91%.

(b) Under a dinitrogen atmosphere a dmf (20 ml) solution of iodine (3.0 g) was added to a dmf (50 ml) solution of bis(salicylaldehyde hydrazone)iron(II) dihydrate (4 g). Bis(salicylaldehyde hydrazone)iron(III) iodide monodimethylformamide separated and isolated as above. The yield of product was 5.0 g, 86%.

*Preparation of Bis(salicylaldehyde hydrazone)-manganese(III) Iodide Monodimethylformamide*

The manganese(III) chelate was isolated in comparable yields as described for the corresponding iron(III) compound using procedure (a) and (b), starting with bis(salicylaldehyde hydrazone)manganese(II) dihydrate.

*Preparation of Bis(salicylaldehyde hydrazone)-chromium(III) Iodide Monohydrate*

A dmf solution (50 ml) containing salicylaldehyde hydrazone (2.1 g) and chromium(III) nitrate hexahydrate (2.7 g) was heated to reflux for 2 h during which time the colour of the solution changed from light green to dark brown. The product of the reac-

tion bis(salicylaldehyde hydrazone)chromium(III) nitrate monohydrate was isolated by addition of water (100 ml), washed with hot ethanol (yield 1.8 g, 90%), and 0.5 g redissolved in hot methanol (100 ml) containing potassium iodide (1 g). The reaction was refluxed for 1 h during which time a light brown product precipitated from solution. After filtration the product was washed with two portions (20 ml) of hot methanol, followed by washing with hot water and air drying at room temperature (yield 0.5 g, 86%). The corresponding chloride, bromide and cyanide derivatives were prepared in comparable yields in the same way, starting from the chromium(III) chelate nitrate.

The elemental analyses and magnetic susceptibility properties of the products are shown by Tables I and II.

**Results**

*Bis(salicylaldehyde hydrazone)iron(III) Iodide*

Tris(salicylaldehyde hydrazone)iron(III) was isolated in good yield from a reaction mixture obtained by adding an ethanol solution of hydrated iron(III) nitrate to an ethanol solution containing

TABLE I. Analytical and Magnetic Susceptibility Data for the Iron and Manganese Chelates with Calculated Values in Brackets

Compound	C (%)	H (%)	N (%)	I (%)	$\mu_{\text{eff}}$ (BM)
Fe(II)(salhy) <sub>2</sub> ·2H <sub>2</sub> O	46.58 (46.43)	5.00 (4.97)	15.40 (15.48)		5.03
Fe(III)(salhy) <sub>3</sub>	54.65 (54.68)	4.55 (4.56)	18.20 (18.23)		5.96
Fe(III)(salhy) <sub>2</sub> I·dmf	38.56 (38.80)	4.05 (3.99)	13.50 (13.31)	24.25 (24.15)	5.86
Mn(II)(salhy) <sub>2</sub> ·2H <sub>2</sub> O	46.50 (46.55)	5.02 (4.98)	15.50 (15.52)		6.03
Mn(III)(salhy) <sub>2</sub> I·dmf	38.75 (38.86)	4.05 (4.00)	13.25 (13.33)	24.50 (24.19)	5.15

TABLE II. Analytical and Magnetic Susceptibility Data for the Chromium(III) Chelates with Calculated Values in Brackets

Compound	C (%)	H (%)	N (%)	X (%) <sup>a</sup>	$\mu_{\text{eff}}$ (BM)
Cr(III)(salhy) <sub>2</sub> NO <sub>3</sub> ·H <sub>2</sub> O	41.90 (41.79)	4.05 (3.98)	17.50 (17.41)		3.75
Cr(III)(salhy) <sub>2</sub> ·I·H <sub>2</sub> O <sup>b</sup>	35.76 (35.95)	3.50 (3.45)	12.10 (11.99)	27.30 (27.19)	3.79
Cr(III)(salhy) <sub>2</sub> ·Cl·H <sub>2</sub> O <sup>c</sup>	44.88 (44.74)	4.38 (4.26)	15.02 (14.91)	9.60 (9.45)	3.85
Cr(III)(salhy) <sub>2</sub> ·Br·H <sub>2</sub> O <sup>d</sup>	40.50 (40.35)	3.86 (3.81)	13.30 (13.33)	19.11 (19.05)	3.74
Cr(III)(salhy) <sub>2</sub> ·CN·H <sub>2</sub> O	49.37 (49.18)	4.55 (4.37)	19.30 (19.12)		

<sup>a</sup>X = I<sup>b</sup>, Cl<sup>c</sup>, Br<sup>d</sup>.

salicylaldehyde hydrazone and triethylamine. When the deep red-brown solution of the iron(III) hydrazone chelate in dimethylformamide (dmf) solution is treated with a dmf solution in hydrazine under dinitrogen atmosphere, the colour of the solution changes to a chocolate colour. The addition of methyl iodide to this solution maintaining a dinitrogen atmosphere results in the precipitation of a light brown product whose elemental analysis corresponds to the composition as bis(salicylaldehyde hydrazone)iron(III) iodide where the iron(III) centre is in a high spin state. The salicylaldehyde hydrazone released from the original tris(salicylaldehyde hydrazone)iron(III) as a result of its conversion to the iodide was recovered in good yield (85%) from the dmf filtrate and characterized by melting point and IR spectroscopy.

ESR spectroscopy provides a convenient method for monitoring the chemical changes which occur during the formation of the iodide. Thus the ESR spectrum due to a frozen (77 K) dmf solution containing tris(salicylaldehyde hydrazone)iron(III) is illustrated by Fig. 1. This rather complicated ESR spectral result simplifies to that shown by Fig. 2 obtained as a result of adding pyridine (5% v/v) to the

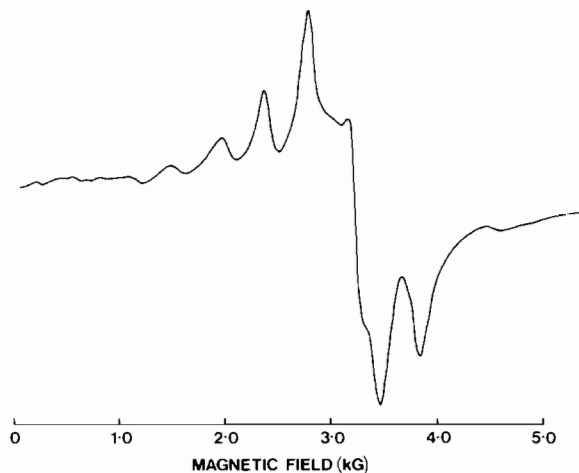


Fig. 1. First derivative ESR spectrum of a frozen dmf solution at 77 K due to  $\text{Fe(III)(salhy)}_3$  ( $3.0 \times 10^{-3} \text{ mol dm}^{-3}$ ). Microwave frequency 9.130 GHz.

dmf solution of tris(salicylaldehyde hydrazone)iron(III) and is attributable to a low spin iron(III) form of the chelate. The ESR spectrum obtained from a frozen (77 K) dmf solution containing tris(

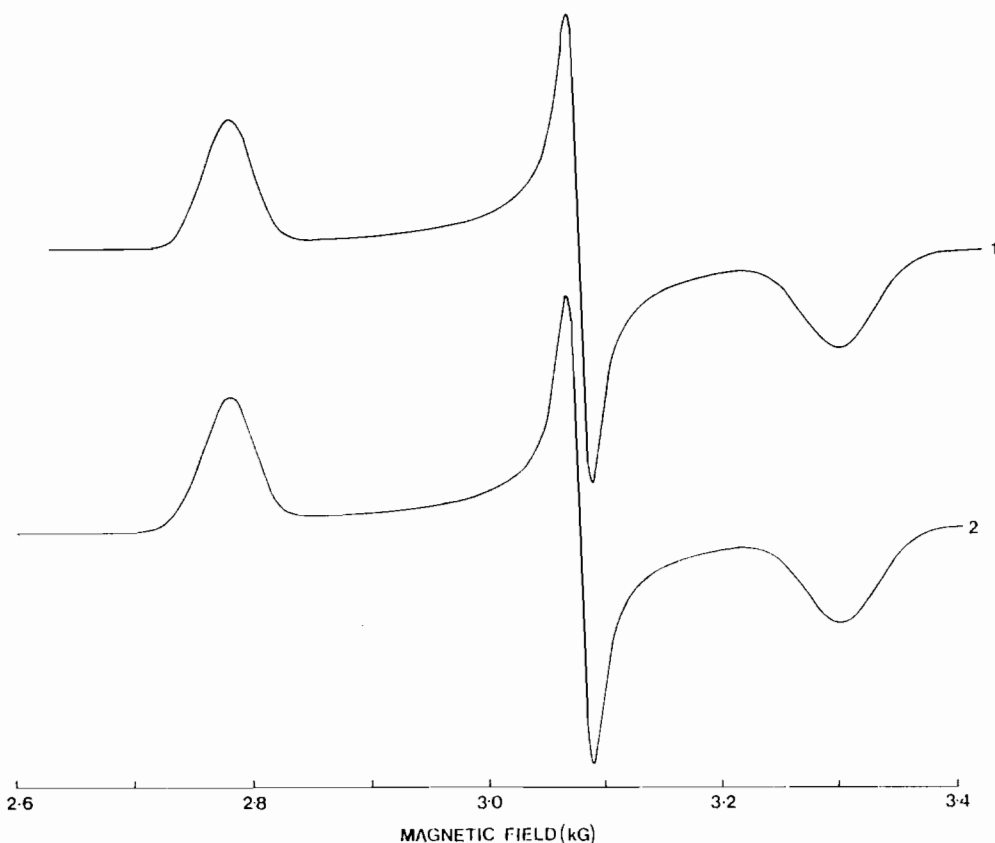


Fig. 2. (1) First derivative ESR spectrum of a frozen dmf solution at 77 K due to  $\text{Fe(III)(salhy)}_3$  ( $3.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) containing 5% (v/v) pyridine. Microwave frequency 9.108 GHz. (2) Computed lineshape using parameters outlined in text.

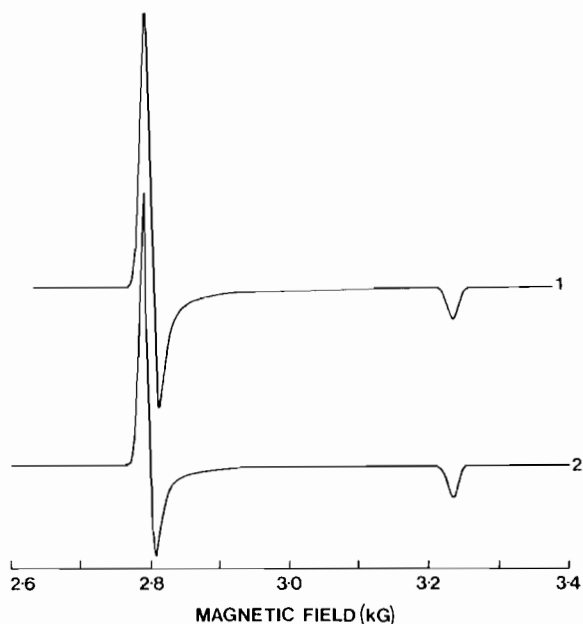


Fig. 3. (1) First derivative ESR spectrum of a frozen dmf solution at 77 K due to  $\text{Fe(III)(salhy)}_3$  ( $3.0 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ) containing a 5-fold excess of hydrazine hydrate under dinitrogen atmosphere. Microwave frequency 9.108 GHz. (2) Computed lineshape.

salicylaldehyde hydrazone)iron(III) and hydrazine hydrate is depicted by Fig. 3 and is recognised as due to an iron(I) chelate. Its similarity to the ESR spectrum exhibited by an iron(I) chelate of a phthalocyanine derivative as outlined later suggests that the spectrum shown by Fig. 3 is due to a bis(salicylaldehyde hydrazone)iron(I) chelate whose oxidative addition reaction with methyl iodide leads to the formation of bis(salicylaldehyde hydrazone)iron(III) iodide, which may also be prepared by addition of a dmf solution of iodine to one containing bis(salicylaldehyde hydrazone)iron(II) under an atmosphere of dinitrogen.

#### *Bis(salicylaldehyde hydrazone)manganese(III) Iodide*

The addition, under an atmosphere of dinitrogen, of hydrazine hydrate to a dmf solution of bis(salicylaldehyde hydrazone)manganese(II) followed by an addition of methyl iodide leads to the precipitation of reddish brown product which was washed with acetone and water. The elemental analysis of the manganese compound points to the composition as being bis(salicylaldehyde hydrazone)manganese(III) iodide monohydrate. The sequence of chemical changes which lead to the formation of this product is revealed by recording the ESR spectrum of the frozen (77 K) dmf solution after each addition of reagents. The ESR spectrum due to a frozen dmf solution of the starting material, bis(salicylaldehyde hydrazone)manganese(II) dihydrate, as shown by

Fig. 4, consists of a number of resonances which includes a six-line hyperfine component, at  $g$  ca. 2. The addition of an excess of hydrazine hydrate to the dmf solution of the manganese(II) chelate results in the observation of the ESR spectrum shown by Fig. 5 which possesses well-defined  $g_{\perp}$  and  $g_{\parallel}$  regions with hyperfine lines of good resolution. This spectrum is attributable to a low spin  $\text{Mn(0)} (3d^7)$  chelate. This ESR spectrum is also generated by the addition of  $\beta$ -mercaptoethanol to a dmf solution containing bis(salicylaldehyde hydrazone)manganese(II) dihydrate. On the other hand, the use of reducing agents such as hydroxylamine, sodium borohydride and sodium dithionite leads to a colour change of a solution of the manganese(II) chelate from brown to yellow and a complete loss of the ESR signal. It is quite likely that these reducing agents affect the production of a manganese(I) chelate of salicylaldehyde hydrazone. The addition of methyl iodide to a dmf solution containing originally bis(salicylaldehyde hydrazone)manganese(II) and hydroxylamine gave rise to the precipitation from solution of bis(salicylaldehyde hydrazone)manganese(III) iodide which can also be formed by the addition of a dmf solution of iodine to one containing the manganese(II) chelate. The further addition of hydrazine hydrate to a dmf solution containing originally bis(salicylaldehyde hydrazone)manganese(II) and hydroxylamine leads to the observation of the ESR spectrum shown by Fig. 5 showing that the one electron reduction of the manganese(II) chelate which is brought about by addition of hydroxylamine is followed by a further one electron reduction by the hydrazine finally to give the manganese(0) chelate. If either of the reduced forms of the manganese chelate was exposed to the air, the manganese(II) chelate was reformed. An ESR spectroscopic titration of a dmf solution of bis(salicylaldehyde hydrazone)manganese(II) with a dmf solution of hydrazine hydrate performed under dinitrogen atmosphere, illustrated in Fig. 6, showed a progressive fall in the intensity of the resonance peaks in the ESR spectra due to bis(salicylaldehyde hydrazone)manganese(II) becoming difficult to detect at the point where the mole ratio of hydrazine hydrate to manganese chelate reached 1:0.5. Further additions of hydrazine hydrate dmf solution resulted in the appearance of the ESR spectra due to the manganese(0) chelate where the intensities of the spectra reached a maximum when the mole ratio of the reagents reached 1:1.

#### *Bis(salicylaldehyde hydrazone)chromium(III) Iodide*

Heating (150 °C) a dmf solution containing chromium(III) nitrate hexahydrate and salicylaldehyde hydrazone in 1:3 mole ratio for 2 h is marked by a colour change from light green to dark

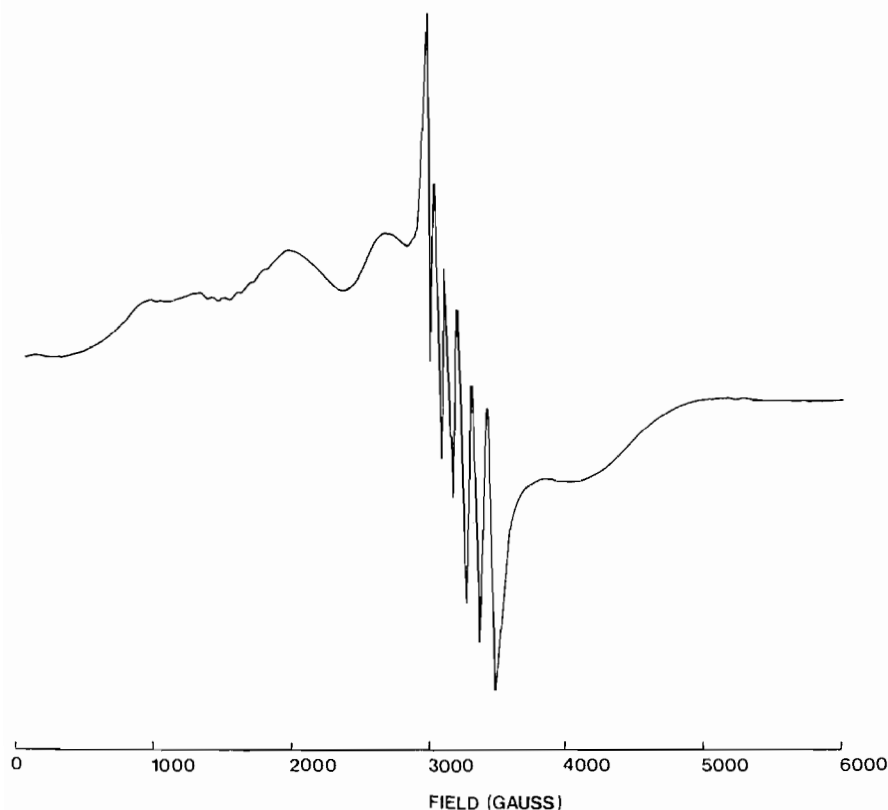


Fig. 4. First derivative ESR spectrum of a frozen dmf solution at 77 K due to  $\text{Mn(II)(salhy)} \cdot 2\text{H}_2\text{O}$  ( $3.0 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ). Microwave frequency 9.147 GHz.

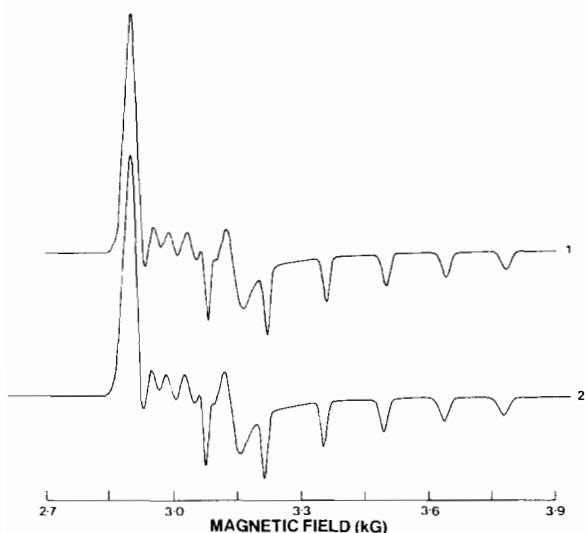


Fig. 5. (1) First derivative ESR spectrum of a frozen dmf solution at 77 K due to  $\text{Mn(II)(salhy)}_2 \cdot 2\text{H}_2\text{O}$  ( $3.0 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ) containing a 5-fold excess of hydrazine hydrate. (2) Computed lineshape.

brown. The product of the reaction, isolated by addition of water to the reaction mixture and washing with ethanol to remove unreacted hydrazone, has an elemental composition pointing to its formulation

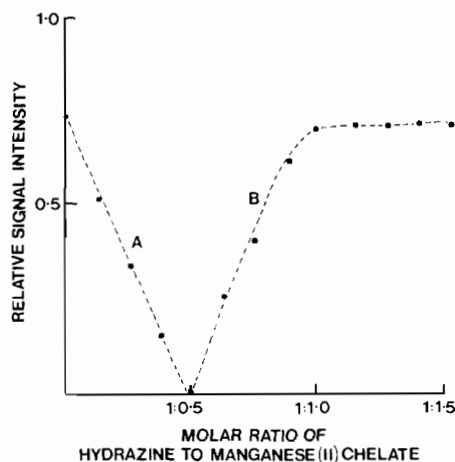


Fig. 6. An ESR spectroscopic titration of a dmf solution of bis(salicylaldehyde hydrazone)manganese(II) dihydrate ( $2.0 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ) with hydrazine hydrate under nitrogen. (a) shows the diminishing relative intensity of the manganese(II) signal measured at  $\sim 3000$  G. (b) shows the rising relative intensity of the manganese(0) signal measured at  $\sim 2910$  G.

as bis(salicylaldehyde hydrazone)chromium(III) nitrate monohydrate.

The corresponding iodide was obtained by heating a methanol solution of the chromium(III) nitrate



Fig. 7. First derivative ESR spectrum of a frozen dmf solution at 77 K of: (1)  $\text{Cr(III)(salhy)}_2 \cdot \text{NO}_3 \cdot \text{H}_2\text{O}$  ( $3.0 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ); (2)  $\text{Cr(III)(salhy)}_2 \cdot \text{I} \cdot \text{H}_2\text{O}$ ; (3)  $\text{Cr(III)(salhy)}_2 \cdot \text{CN} \cdot \text{H}_2\text{O}$ ; (4)  $\text{Cr(III)(salhy)}_2 \cdot \text{SCN} \cdot \text{H}_2\text{O}$ . Microwave frequency 9.136 GHz.

chelate containing potassium iodide. Precipitate formed was filtered and washed with hot methanol to remove unreacted starting material. Using similar procedures, bis(salicylaldehyde hydrazone)chro-

mium(III) chloride and cyanide were prepared. Each product is characterized by its ESR spectrum in dmf as shown by Fig. 7. The ESR spectra show peaks over a 5000 Gauss range with a sharper resolution than those observed by Pedersen and Toftlund [4].

#### Interpretation of the ESR Spectral Data

##### (a) Low spin forms of the iron(III) and iron(I) chelates

The ESR spectrum due to the low spin iron(III) chelate observed in dmf containing pyridine as well as that due to the low spin iron(I) chelate obtained after addition of hydrazine may be accounted for by a spin Hamiltonian of the form:

$$\mathcal{H} = \beta \sum_{i=x, y, z} g_i S_i B_i \quad (1)$$

Computer simulations of the ESR spectrum due to the low spin form of tris(salicylaldehyde hydrazone)iron(III) monopyridine and iron(I) salicylaldehyde hydrazone chelate were achieved using the values of the spin Hamiltonian parameters and linewidth terms shown by Table III. The values of  $g_{\parallel}$  and  $g_{\perp}$  which characterize the iron(I) chelate are close to those found for the iron(I) chelate of 3,10,17,24-tetrasulphonatophthalocyanine [5] which suggests strongly that the iron(I) chelate possesses a planar  $\text{N}_2\text{O}_2$  donor set provided by two salicylaldehyde hydrazone ligands. The  $g_z$  values obtained from the low spin iron(III) form of the hydrazone chelate is less than that observed in low spin 3,10,17,24-tetrasulphonatophthalocyaninato ferrate(III) ( $g_x = 1.830$ ,  $g_y = 2.250$ ;  $g_z = 2.575$ ) [5] or in low spin dimethoxy(5,10,15,20-tetra-phenylporphyrinato)-ferrate(III) ( $g_x = 1.914$ ;  $g_y = 2.165$ ;  $g_z = 2.494$ ) [6].

The background theory for low spin  $d^5$  has been summarized at length previously [7].

Recent improved understanding of the nature of field-swept ESR spectra show their computer simulation should be considered as follows [8, 9]: The spin Hamiltonian is solved at various frequencies and the resonance frequency difference,  $\nu_o(B)$ , as a function of the magnetic field, is determined at each point across a line where at the line centre  $\nu_o(B) = \nu_c$  (the constant applied frequency). The detected absorption signal is proportional to

$$S(B) = \sum_{\theta} \sum_{\phi} \sum_{M_I = -1}^1 g_1^2 f(\nu_c - \nu_o[B], \sigma_\nu) \quad (2)$$

$g_1^2$  is the powder averaged intensity factor due to anisotropy. Here the lineshape is defined in frequency space, and the linewidth,  $\sigma_\nu$ , given in frequency units. The first derivative of  $S(B)$  is obtained by numerical differentiation. For low spin Fe(III),  $I = 0$  and no hyperfine structure is involved whereas for Mn(II), to be discussed later,  $I = 5/2$ .

TABLE III. The Spin Hamiltonian Parameters for the Iron(III) and Iron(I) Chelates in a Frozen dmf Solution at 77 K<sup>a</sup>

Compound	$g_x$	$g_y$	$g_z$	$\sigma_{Rx}$ (MHz)	$\sigma_{Ry}$ (MHz)	$\sigma_{Rz}$ (MHz)
Fe(III)(salhy) <sub>3</sub> ·py <sup>b</sup>	1.940	2.080	2.300	30	8	20
Fe(I)salhy chelate <sup>c</sup>	2.324	2.324	2.013	7	7	8

<sup>a</sup>Fitting errors:  $g (\pm 0.001)$ ;  $\sigma (\pm 1)$ . <sup>b</sup>Formed by the addition of 5% (v/v) of pyridine to Fe(III)(salhy)<sub>3</sub> in dmf. <sup>c</sup>Formed by the addition of an excess of hydrazine hydrate (5-fold excess) to Fe(III)(salhy)<sub>3</sub> in dmf.

Equation (2) differs from the usual representation of ESR spectra where the shape function is written in terms of magnetic field variables but, for accurate simulation, must be divided by the  $g$ -factor appropriate to each line centre.

The angular variation of the linewidth is treated in the same manner as hyperfine structure so that

$$\sigma_\nu^2 = \sum_{i=x,y,z} \sigma_{\nu i}^2 l_i^2 \quad (3)$$

where the  $l_i$  values ( $i = x, y, z$ ) are the direction cosines of the magnetic field with respect to the  $g$ -axes.

In general  $\sigma_\nu$  depends on a residual component,  $\sigma_R$  due to spin-spin broadening or unresolved ligand hyperfine structure and effects due to distribution of  $g$ - and  $A$ -values. For the Fe(III) cases here (Table 3)  $\sigma_\nu = \sigma_R$ , no particular dependence upon the so-called 'g-strain' proved necessary.

(b) Low spin form of the manganese(0) chelate

The ESR spectrum due to the manganese(0) form of the hydrazone chelate is due to a spin 1/2 ion ( $3d^7$ ) in an environment having axial symmetry may be represented by the spin Hamiltonian

$$\mathcal{H} = \beta [g_{\parallel} B_z S_z + g_{\perp} (B_x S_x + B_y S_y)] + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y) \quad (4)$$

where  $B$  is the magnetic field and other parameters have their usual meanings. A computer simulation of the ESR spectrum due to the low spin manganese(0) hydrazone chelate was achieved using values of the spin Hamiltonian parameters and linewidth terms out-

TABLE IV. The Spin Hamiltonian Parameters for the Manganese(0)salhy Chelate in Frozen dmf Solution at 77 K<sup>a</sup>

Compound	Hyperfine constants			
	$g_{\perp}$	$g_{\parallel}$	$A_{\perp}$ ( $\times 10^{-4}$ cm <sup>-1</sup> )	$A_{\parallel}$ ( $\times 10^{-4}$ cm <sup>-1</sup> )
Mn(0)salhy chelate <sup>b</sup>	2.130	1.880	43	124
Mn(0)salhy chelate <sup>c</sup>	2.125	1.865	40	120

<sup>a</sup>Fitting errors:  $g (\pm 0.001)$ ,  $A_{\parallel} (\pm 1)$ ,  $A_{\perp} (\pm 2)$ . <sup>b</sup>Formed by the addition of an excess of hydrazine hydrate (5-fold excess) to manganese(II)(salhy)<sub>2</sub>·2H<sub>2</sub>O in dmf. <sup>c</sup>Formed by the addition of an excess of  $\beta$ -mercaptoethanol (7-fold excess) to manganese(II)(salhy)<sub>2</sub>·2H<sub>2</sub>O in dmf.

lined by Tables IV and V respectively. The derivation of the linewidth terms  $\sigma_{Ri}$ ,  $\sigma_{R\parallel}$ ,  $C_{\perp\perp}$ ,  $C_{\perp\parallel}$ ,  $C_{2\perp}$  and  $C_{2\parallel}$  has been outlined recently [10, 11] and is based on the principal value of the linewidth defined as

$$\sigma_{\nu i} = \{ \sigma_{Ri}^2 + (C_{1i} \nu_o [B] - C_{2i} M_I)^2 \}^{1/2} \quad (5)$$

where  $i = \parallel$  or  $\perp$  (or  $x, y$  and  $z$ ),  $\sigma_{Ri}$  is the residual width mentioned previously, and

$$C_{1i} = \sigma_{gi}/g_i \quad (6a)$$

and

$$C_{2i} = \sigma_{Ai} \quad (6b)$$

In eqn. (6)  $\sigma_{gi}$  and  $\sigma_{Ai}$  should be considered to be the variances of the random distributions of  $g_i$  and  $A_i$  values treated as random variables. If imperfect correlation exists then in eqn. (5),

$$(C_{1i} \nu_o [B] - C_{2i} M_I)^2$$

TABLE V. Linewidth Terms for the Manganese(0)salhy Chelate in dmf at 77 K<sup>a</sup>

Compound	$\sigma_{R\perp}$ (MHz)	$\sigma_{R\parallel}$ (MHz)	$C_{\perp\perp}$	$C_{\perp\parallel}$	$C_{2\perp}$ (MHz)	$C_{2\parallel}$ (MHz)
Mn(0)salhy chelate <sup>b</sup>	24	16	0.0008	0.0015	3.2	4.7
Mn(0)salhy chelate <sup>c</sup>	27	17	0.0004	0.0014	3.0	5.1

<sup>a</sup>Fitting errors:  $\sigma_R \approx \pm 1$ ;  $C_1 \approx \pm 0.0001$ ;  $C_2 \approx \pm 0.2$ .

excess) to manganese(II)(salhy)<sub>2</sub>·2H<sub>2</sub>O in dmf.

manganese(II)(salhy)<sub>2</sub>·2H<sub>2</sub>O in dmf.

<sup>b</sup>Formed by the addition of an excess of hydrazine hydrate (5-fold excess) to manganese(II)(salhy)<sub>2</sub>·2H<sub>2</sub>O in dmf.

<sup>c</sup>Formed by the addition of an excess of  $\beta$ -mercaptoethanol (7-fold excess) to

should be multiplied out and the cross term multiplied by a correlation coefficient,  $\rho_i$  where  $|\rho_i| \leq 1$ . This has not been found necessary here.

The values of the spin Hamiltonian parameters obtained here are to some extent dependent on the reducing agent used and presumably arises from axial interactions with the excess of reagent present in each case. However, both sets of values are close to those obtained for the manganese(0) chelate of 3,10,17,24-tetrasulphonatophthalocyanine ( $g_{\parallel} = 1.865$ ,  $g_{\perp} = 2.125$ ,  $A_{\parallel} = 140 \times 10^{-4} \text{ cm}^{-1}$ ,  $A_{\perp} = 50 \times 10^{-4} \text{ cm}^{-1}$ ) pointing to planar  $\text{N}_2\text{O}_2$  donor set in the hydrazone chelate arising from ligation by two salicylaldehyde hydrazone ligands.

With regard to the  $d^7$  low spin Mn(0) configuration resulting from the two-electron reduction of the Mn(II) chelate, several points must be made. Evidence for low spin Mn(0) based solely on  $g$ - and  $A$ -values is insufficient. Here as in a previous result [12] the conclusion depends on a consideration of UV-Vis titration data with strong reducing agents and the internal self-consistency of the spin Hamiltonian data. It was previously argued that the  $g$ -values and absence of axial ligand hyperfine structure would result from a  $d_{xy}$  orbital ground state. This might also explain  $g_{\parallel} = 1.80$  for the iodocobinamide complex [13].

## Discussion

The compounds of the type bis(salicylaldehyde hydrazone)M(III) iodide are obtained in good yields by the oxidative pathways involving the addition of methyl iodide or iodine to their reduced forms. In the case of the chromium(III) chelate, the stability of the bis form with its  $\text{O}_2\text{N}_2$  equatorial donor set is favoured over the tris form. The stability of the bis(salicylaldehyde hydrazone)chromium(III) iodide monohydrate has repercussions in considering the stereochemistry of the hydrazone chelates of iron and manganese. Thus, although tris(salicylaldehyde hydrazone)iron(III) is stable, the

third hydrazone ligand makes way for the addition of pyridine to form a low spin iron(III) form whose six-coordination is made up of an equatorial  $\text{N}_2\text{O}_2$  donor set with pyridine nitrogen and a nitrogen from the hydrazone ligand occupying the axial positions. The equatorial donor set  $\text{O}_2\text{N}_2$  persists in the iron(I) form of the chelate where, remarkably, the electronic environment of the metal ion is comparable to that of a macrocyclic  $\text{N}_4$  donor set. The oxidative addition of iodide from methyl iodide would involve minimal stereochemical change to form the bis(salicylaldehyde hydrazone)iron(III) iodide where a solvent molecule completes the six-coordination. Again, in the reduced form of the manganese chelates which, in the case of the manganese(0) form the ESR, spectroscopic evidence points to a stable planar macrocyclic-like environment which gives rise to the manganese(III) form by oxidative addition.

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