Chemistry of Ferroverdin: Trinuclear Species of Type $[M(FeL_3)_2]$ [M = Mg, Ca, Mn, Fe, Co, Ni, Zn, or Cd; L = 4-methyl-1,2-benzoquinone 2-oximate)

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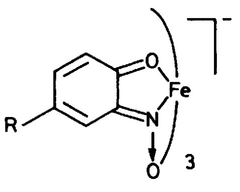
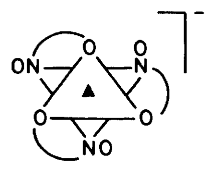
Reaction of sodium tris(4-methyl-1,2-benzoquinone 2-oximato)ferrate(II), $Na[FeL_3]$, with M^{2+} (M = Mg, Ca, Mn, Fe, Co, Ni, Zn, or Cd) in methanol furnishes trinuclear species of type $[M(FeL_3)_2]$. Upon treatment with NaOH, $M(OH)_2$ is precipitated and $Na[FeL_3]$ is regenerated. The iron(II) atoms of the two $[FeL_3]^-$ moieties in the trinuclear complexes are low spin but M^{2+} is high spin ($S = \frac{5}{2}, 2, \frac{3}{2}$, and 1 in the cases of M = Mn, Fe, Co, and Ni respectively). The M^{2+} site can be doped with Mn^{2+} and e.s.r. data for the doped complexes are compatible with a near octahedral environment of the M^{2+} site. It is proposed that this environment is created by the six oximato oxygen atoms of the two facial $[FeL_3]^-$ moieties. The significance of the present work in relation to the reported variation of the iron content in different preparations of ferroverdin is noted.

A green pigment ferroverdin, is generated by a species of *Streptomyces* in submerged cultures containing iron salts.[1] A single-crystal *X*-ray crystallographic study[2] of one preparation demonstrated that it contains the tris chelate anion (**1**) in the facial configuration (**2**) and the counter cation is Na^+ [R = *p*-$(CH_2{=}CH)C_6H_4OC({=}O)$–]. The bivalent iron is in the low-spin ($S = 0$) state.[1b] The ligand in (**1**) is designated as a 1,2-quinone 2-oximate rather than a nitrosophenolate.[3,4]



(**1**)



(**2**)

Different preparations of ferroverdin however differed in iron content and it was conjectured that this is due to counter-cation variation or due to decomposition.[2] The present work was undertaken to examine the nature and extent of such variation. A synthetic analogue $Na[FeL_3]$ (**1**; R = Me) of ferroverdin prepared by nitrosation of *p*-cresol in the presence of iron(II) sulphate[5] has been used for this purpose. It is demonstrated that bivalent cations (M^{2+}) readily displace Na^+ from $Na[FeL_3]$ and afford species of type $[M(FeL_3)_2]$. The nature and properties of these trinuclear species are reported.

Results and Discussion

Reaction of $Na[FeL_3]$ *with Bivalent Cations* (M^{2+}): $[M(FeL_3)_2]$.—Under ambient conditions green methanolic solutions of $Na[FeL_3]$ smoothly react with salts of numerous bivalent ions, equation (1). The colour of the solution rapidly changes to bluish green and the sparingly soluble trinuclear complex precipitates as a dark coloured solid. The colour change can be used to diagnose whether a particular M^{2+} is active or not. The ions Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} successfully afforded $[M(FeL_3)_2]$ complexes but Sr^{2+} and Ba^{2+} failed to react.

$$2Na[FeL_3] + M^{2+} \longrightarrow [M(FeL_3)_2] + 2Na^+ \quad (1)$$

Selected characterisation data for the complexes are given in the Table. Their osmometric molecular weights in $CHCl_3$ solution are in full accord with the trinuclear formulation. The complexes with M = Mg, Ca, Zn, or Cd are diamagnetic showing that the two iron(II) atoms in $[M(FeL_3)_2]$ like that[5] in $Na[FeL_3]$ are low spin. The magnetic moments of the complexes with M = Mn, Fe, Co, or Ni correspond to high-spin M^{2+} ($S = \frac{5}{2}, 2, \frac{3}{2}$, and 1 respectively). Thus in $[Fe(FeL_3)_2]$ iron(II) is present in two spin states. Like $Na[FeL_3]$,[5] the trinuclear complexes absorb strongly around 700 nm but the band is characteristicly split into two components (Figure 1).

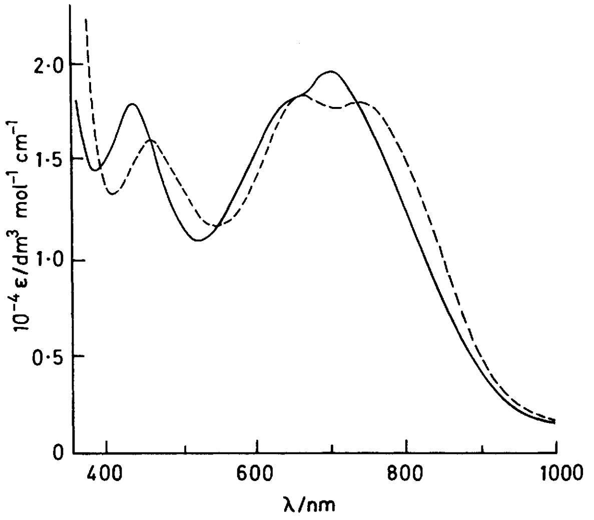


Figure 1. Electronic spectra of $[Ca(FeL_3)_2]$ (——) and $[Fe(FeL_3)_2]$ (– – –) in dichloromethane

Thus the conjecture that Na^+ in different ferroverdin preparations 'may be replaced by other ions, even perhaps sometimes by additional ferrous ion'[2] is justified and it is not necessary to invoke 'partial decomposition'[2] to rationalise compositional variations. We note that the empirical formula of $[Fe(FeL_3)_2]$ is simply FeL_2 and this composition was proposed for one ferroverdin preparation.[1c]

Regeneration of $Na[FeL_3]$.—Treatment of $[M(FeL_3)_2]$ in acetone solution with aqueous NaOH in mole ratio 1:2 leads to quantitative precipitation of $M(OH)_2$ and reformation of

Table. Characterisation data for the $[M(FeL_3)_2]$ complexes

M	Analysis[a] (%) M	Fe	C	H	N	$M^{a,b}$	$\mu_{eff.}$[c]	U.v.–visible spectral data,[d] $\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})
Mg	2.4	11.6	52.5	3.7	8.7	917	*e*	700 (20 700), 660 (20 600),
	(2.6)	(11.7)	(52.9)	(3.8)	(8.8)	(952.02)		440 (15 950), 325 (33 800)
Ca	4.0	11.4	51.8	3.9	8.5	1 010	*e*	700 (19 600), 630[f] (17 200),
	(4.1)	(11.5)	(52.1)	(3.7)	(8.7)	(967.78)		440 (17 800), 330 (38 650)
Mn	5.6	11.5	51.4	3.8	8.3	1 017	5.73	740 (18 250), 660 (19 650),
	(5.6)	(11.4)	(51.3)	(3.7)	(8.6)	(982.64)		450 (14 900), 330 (29 300)
Fe	5.6	11.4	51.3	3.7	8.2	1 020	4.93	745 (17 950), 660 (18 300),
	(5.7)	(11.4)	(51.2)	(3.7)	(8.5)	(983.55)		460 (15 800), 340 (32 100)
Co	5.7	11.4	50.9	3.8	8.8	973	4.44	760 (21 500), 650 (20 900),
	(6.0)	(11.3)	(51.1)	(3.7)	(8.5)	(986.63)		470 (16 000), 340 (27 400)
Ni	5.8	11.2	51.1	3.8	8.7	964	3.18	755 (23 800), 650 (21 500),
	(6.0)	(11.3)	(51.1)	(3.7)	(8.5)	(986.41)		475 (14 750), 340 (28 500)
Zn	6.6	11.0	50.8	3.8	8.4	933	*e*	740 (18 800), 650 (19 500),
	(6.6)	(11.3)	(50.8)	(3.6)	(8.5)	(993.07)		450 (14 750), 330 (27 900)
Cd	10.7	10.9	48.3	3.5	8.3	1 022	*e*	740 (18 400), 660 (20 300),
	(10.8)	(10.7)	(48.5)	(3.5)	(8.1)	(1 040.10)		445 (16 800), 335 (31 100)

[a] Calculated values are in parentheses. [b] In chloroform. [c] At 298 K. [d] In dichloromethane. [e] Diamagnetic. [f] Shoulder.

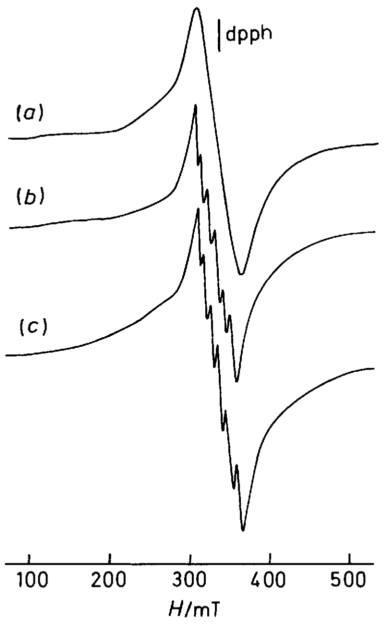
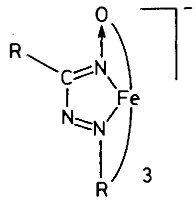


Figure 2. *X*-Band e.s.r. spectra at 298 K of polycrystalline (*a*) $[Mn(FeL_3)_2]$, (*b*) $[(Mg,Mn)(FeL_3)_2]$, and (*c*) $[(Fe,Mn)(FeL_3)_2]$

$Na[FeL_3]$, equation (2). The hydroxide remains partially or fully in solution only in the case of calcium. Taken collectively, the reactions (1) and (2) strongly suggest that no fundamental change occurs to the $Fe^{II}L_3$ moiety in course of its association with cations.

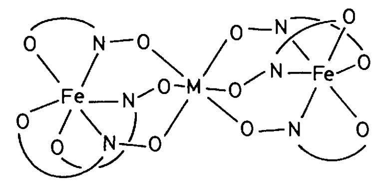
$$[M(FeL_3)_2] + 2NaOH \longrightarrow M(OH)_2 + 2Na[FeL_3] \quad (2)$$

Structure.—We have not succeeded so far in growing *X*-ray-quality single crystals of any of the $[M(FeL_3)_2]$ complexes and therefore their molecular structure remains uncertain. However a plausible suggestion can be made on the basis of analogy with iron arylazo-oximates.[6] The anion $[FeL'_3]^-$ (**3**), like (**1**), is facial and also affords trinuclear $[M(FeL'_3)_2]$ which have been structurally characterised.[6b,c] Each facial $[FeL'_3]^-$ moiety acts as a tridentate O_3 (oximato oxygen atoms) ligand and the M^{2+} ion is held in the octahedral O_6 co-ordination sphere created by two such ligands; the FeMFe sequence is essentially linear. We propose that $[M(FeL_3)_2]$ complexes are similarly constituted as shown in (**4**). The observed high-spin nature of the M^{2+} in the complexes is in accord with (**4**) since the oximato oxygen atoms have a weak ligand field.[6c]



(3)

R = aryl



(4)

The formation of $[M(FeL_3)_2]$ from $[FeL_3]^-$ and M^{2+} [equation (1)] and its cleavage by alkali [equation (2)] finds ready rationalisation in structure (**4**). In equation (1) two molecules of the ligand moiety $[FeL_3]^-$ are neatly assembled by M^{2+} to provide octahedral co-ordination and in equation (2) the OH^- ion displaces the ligands forming insoluble hydroxides.

In *X*-band e.s.r. spectra of polycrystalline $[Mn(FeL_3)_2]$ as well as all other $[M(FeL_3)_2]$ doped with 1% manganese(II) {the doped complexes are designated by $[(M,Mn)(FeL_3)_2]$} a strong resonance is observed at $g \approx 2$. Spectra were measured at 298 and 77 K but there was little change in the resonance pattern. Representative spectra are shown in Figure 2. The pure complexes with M = Fe, Co, or Ni are themselves paramagnetic but do not display any e.s.r. signals of their own evidently due to rapid relaxation.

For pure $[Mn(FeL_3)_2]$ the $g \approx 2$ resonance is relatively broad presumably due to exchange broadening. With the doped complexes this complication is removed through dilution and the six-line ^{55}Mn hyperfine structure is neatly resolved (average A = 95 G, 9.5 × 10^{-3} T). In frozen (77 K) dilute solution in dichloromethane, $[Mn(FeL_3)_2]$ displays a similar hyperfine resolution. For six-co-ordinated high-spin manganese(II) a strong resonance at $g \approx 2$ implies an exactly or nearly octahedral environment.[6c,d,7] It is logical to assume that in the doped complexes manganese(II) partly substitutes for metal(II) in the lattice. If the manganese(II) occurred as a separate phase outside the host lattice, it would have afforded a spectrum without hyperfine structure like that of the pure manganese(II) complex.[8] The present results therefore suggest that all the $[M(FeL_3)_2]$ have very similar environments for M which are probably nearly octahedral.

The radii of the ions utilised in the present work for trinucleation span the range[9] 0.68—1.06 Å. The radii of Sr^{2+} (1.27 Å) and Ba^{2+} (1.43 Å) which fail to afford $[M(FeL_3)_2]$ are larger. The significance of this is unclear at present but it may be related to the viable size of the octahedral O_6 cavity.

Experimental

Starting Materials.—Hydrated perchlorates of iron(II) and other metals(II) were prepared by dissolving iron powder and the corresponding metal carbonates in 70% aqueous perchloric acid followed by recrystallisation. All other chemicals and solvents used were of reagent grade.

Physical Measurements.—Molecular weights were determined by using a Knauer vapour-pressure osmometer with benzil as calibrant. Microanalytical data (C, H, and N) were obtained with a Perkin-Elmer model 240C elemental analyser. Magnetic susceptibilities were measured on a PAR-155 vibrating-sample magnetometer fitted with a Walker Scientific magnet. *X*-Band e.s.r. spectra were recorded on a Varian E-109C spectrometer fitted with a quartz Dewar for measurements at 77 K (liquid nitrogen). The spectra were calibrated with respect to diphenylpicrylhydrazyl (dpph) (g = 2.0037). Electronic spectra were recorded using a Hitachi 330 spectrophotometer.

$[Mn(FeL_3)_2]$.—To a solution of $Na[FeL_3]$ (0.50 g, 1.03 mmol) in methanol (25 cm^3) was added $Mn(ClO_4)_2 \cdot 6H_2O$ (0.20 g, 0.56 mmol) and the mixture was stirred magnetically at room temperature for 1 h. The initial green colour of the solution changed immediately to bluish green and a dark solid precipitated. The compound was collected by filtration, washed thoroughly with methanol followed by water, and dried *in vacuo* over P_4O_{10} (yield 85%).

All other trinuclear complexes reported in this work were prepared by using the procedure described above from $Na[FeL_3]$ and the corresponding metal(II) perchlorate hexahydrate.

Doped Complexes, $[(M,Mn)(FeL_3)_2]$ (M = Mg^{II}, Ca^{II}, Fe^{II}, Co^{II}, Ni^{II}, Zn^{II}, *or* Cd^{II}).—These were prepared from $Na[FeL_3]$ and hydrated $M(ClO_4)_2$ containing 1% $Mn(ClO_4)_2 \cdot 6H_2O$ following the procedure described above for the synthesis of the pure complex.

Reaction of $[M(FeL_3)_2]$ *with* NaOH.—To a solution of the complex in acetone was added an aqueous solution of sodium hydroxide (the mole ratio of complex to NaOH was 1:2). The mixture was warmed and stirred for 0.5 h. The green solution was filtered to remove the precipitated metal hydroxide and the filtrate was concentrated. Shiny dark crystals separated and were collected by filtration. The compound thus obtained was dried *in vacuo* over P_4O_{10} and characterised as $Na[FeL_3]$.

The precipitated metal hydroxide was estimated quantitatively using standard methods. In the above reaction 1 mol of $[M(FeL_3)_2]$ produced 1 mol of $M(OH)_2$ (Table).

Acknowledgements

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