Tripodal Benzimidazolate Complexes of Tricarbonylmolybdenum(0) and of Iron(III)

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The reactions of the tripodal ligands *N,N*-bis(benzimidazol-2-ylmethyl)amine (L^1), *N,N*-bis(benzimidazol-2-ylmethyl)methylamine (L^2), and *N,N*-bis(1-methylbenzimidazol-2-ylmethyl)methylamine (L^3) with molybdenum hexacarbonyl and tris(acetonitrile)tricarbonylmolybdenum to give (benzimidazolato)tricarbonylmolybdenum complexes, and of L^1 and L^3 with iron(III) salts to give di-iron(III) complexes containing the $[Fe_2(\mu\text{-O})(\mu\text{-RCO}_2)_2]^{2+}$ core are described. The application of the molybdenum complexes as i.r. spectroscopic probes for the ligand bands in the dinuclear species is reported, together with the mass spectra and electronic spectra of the di-iron(III) species. The di-iron(III) complexes show an ability to undergo carboxylate exchange reactions.

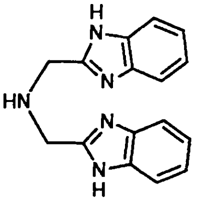
The study of complexes bearing the $[Fe_2(\mu\text{-O})(\mu\text{-RCO}_2)_2]^{2+}$ core has been proposed as an aid to the understanding of the design and assembly of the dinuclear cores present in metalloproteins such as haemerythrin, methane mono-oxygenase, and ribonucleotide reductase.[1] In this paper we report on three tripodal benzimidazolate complexes of tricarbonylmolybdenum(0), which have been synthesised and used as i.r. spectroscopic probes in order to facilitate the assignment of the ligand and Fe–O–Fe frequencies in a number of di-iron(III) complexes (**14**)—(**25**). The latter have been characterised, by use of i.r., electronic, and mass spectra, and shown to undergo carboxylate exchange reactions.

Experimental

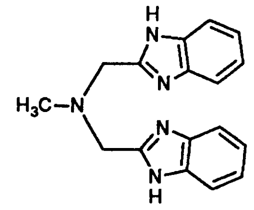
Microanalyses were carried out by the University of Sheffield Microanalytical service. I.r. spectra were recorded as KBr discs using a Perkin-Elmer 297 i.r. spectrophotometer (4 000—600 cm^{-1}) or a Perkin-Elmer 1710 i.r. Fourier-transform spectrophotometer (4 000—400 cm^{-1}), electronic absorption spectra were recorded using a Philips PU8720 u.v.–visible scanning spectrophotometer operating in the range 280—900 nm. ^{1}H N.m.r. spectra were recorded at 220 MHz on a Perkin-Elmer R34 spectrometer and the ^{1}H n.m.r. spectra (250 MHz) of paramagnetic samples and ^{13}C n.m.r. spectra (62.9 MHz) were recorded using a Bruker AM-250 spectrometer. Electron impact (e.i.) mass spectra were recorded on a Kratos MS25 spectrometer operating at low resolution and positive ion fast atom bombardment (f.a.b.) mass spectra were recorded on a Kratos MS80 spectrometer. The matrix used was 3-nitrobenzyl alcohol (noba) unless otherwise stated.

CAUTION: Although no problems were encountered during the preparation of the perchlorate salts described below, suitable care and precautions should be taken when handling such potentially hazardous compounds.

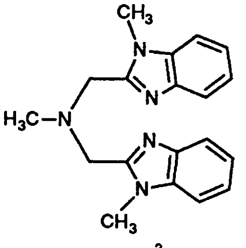
N,N-Bis(benzimidazol-2-ylmethyl)amine (L^1) and *N,N*-bis(benzimidazol-2-ylmethyl)methylamine (L^2) were prepared by a modification of the method of Berends and Stephan.[2–4] The compounds $[FeL^1Cl_3]$ and $[Fe_2L^1_2(\mu\text{-O})(\mu\text{-Me}_3CCO_2)_2][ClO_4]_2$ (**18**) were prepared as in ref. 2.



L^1



L^2



L^3

N,N-*Bis*(1-*methylbenzimidazol*-2-*ylmethyl*)*methylamine* (L^3).—Powdered KOH (2.80 g, 50 mmol) was added to a stirred suspension of L^2 (2.92 g, 10 mmol) in acetone (50 cm^3). The solution was stirred at room temperature for 5 min. Iodomethane (1.40 cm^3, 3.15 g, 22 mmol) was added dropwise with vigorous stirring. The mixture was stirred for a further 15 min, during which time a fine precipitate of KI formed. The solvent was removed under reduced pressure and the residue shaken with a mixture of water (100 cm^3) and CH_2Cl_2 (50 cm^3). Upon dissolution of all the solid, the organic phase was separated and the aqueous phase extracted again with CH_2Cl_2 (50 cm^3). The combined extracts were dried over $MgSO_4$, filtered, and the solvent removed under reduced pressure. The crude product was recrystallised from methanol–water to give white crystals of the monohydrate (2.63 g, 78%), m.p. 220 °C (Found: C, 67.90; H, 6.75; N, 20.80. $C_{19}H_{23}N_5O$ requires C, 67.60; H, 6.90; N, 20.80%); *m*/*z* (chemical ionisation, c.i.) 320 (MH^+, 58%). $\delta_H(CDCl_3)$ 7.70 (2 H, m), 7.19 (6 H, m), 3.78 (4 H, s), 3.50 (6 H, s), and 2.26 (3 H, s).

Preparation of $Mo(CO)_3$ *Derivatives of* L^1—L^3.—*Method* (*a*). *fac*-$[MoL^1(CO)_3]$ (**1**). Molybdenum hexacarbonyl (0.26 g, 1 mmol) and $L^1\cdot H_2O$ (0.29 g, 1 mmol) were refluxed gently in acetonitrile (40 cm^3) under nitrogen for 2 h. The initial suspension dissolved to give a yellow solution from which a pale yellow solid precipitated. The mixture was cooled to room temperature and the product filtered off. After washing with acetonitrile, ethanol, and diethyl ether the pale yellow powder was dried in air (0.41 g, 81%) (Found: C, 50.10; H, 3.30; N, 15.60. $C_{19}H_{15}MoN_5O_3$ requires C, 49.90; H, 3.30; N, 15.30%). No f.a.b. mass spectrum was observed. I.r.: ν_{CO} at 1 884s, 1 761s, and 1 723s cm^{-1}.

fac-$[MoL^2(CO)_3]$ (**2**). This was prepared as above (83%) (Found: C, 50.90; H, 3.60; N, 14.80. $C_{20}H_{17}MoN_5O_3$ requires C, 51.00; H, 3.60; N, 14.90%); *m/z* (f.a.b., noba) 473 (M^+, 100%) (strongest peak corresponds to ^{98}Mo, with the expected isotope pattern). I.r.: ν_{CO} at 1 891s, 1 771s, and 1 702s cm^{-1}.

Method (*b*). *fac*-$[MoL^3(CO)_3]$ (**3**). Molybdenum hexacarbonyl (0.26 g, 1 mmol) was refluxed gently in acetonitrile (40 cm^3) for 10 h. Throughout the reaction nitrogen gas was bubbled through the solution to remove CO gas. The air-sensitive, clear, yellow solution of $[Mo(CO)_3(MeCN)_3]$ was allowed to cool (MeCN solution: ν_{CO} at 1 921s and 1 793vs cm^{-1}). Then $L^3{\cdot}H_2O$ (0.34 g, 1 mmol) was added and the solution refluxed for 2 h. The light yellow microcrystalline product was filtered off, washed with acetonitrile, ethanol, then diethyl ether, and finally dried in air (0.46 g, 92%) (Found: C, 52.50; H, 4.35; N, 14.05. $C_{22}H_{21}MoN_5O_3$ requires C, 52.90; H, 4.20; N, 14.00%); *m/z* (f.a.b., sulpholane) 501 (M^+, 100%) (strongest peak corresponds to ^{98}Mo, with the expected isotope pattern). I.r.: ν_{CO} at 1 890s, 1 763s, and 1 748s cm^{-1}.

Preparation of Iron Complexes.—$[FeL^3Cl_3]$. This was prepared by the method in ref. 2 but using the ligand $L^3{\cdot}H_2O$ (0.34 g, 1 mmol). The reaction was carried out in methanol (40 cm^3). The compound $[FeL^3Cl_3]$ precipitated as a yellow–orange powder (0.41 g, 85%) (Found: C, 47.40; H, 4.50; Cl, 21.90; N, 14.40. $C_{19}H_{21}Cl_3FeN_5$ requires C, 47.40; H, 4.40; Cl, 22.10; N, 14.50%).

$[Fe_2L^1{}_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2]Cl_2{\cdot}0.5H_2O{\cdot}0.5EtOH$ (**14**). Iron(III) chloride hexahydrate (0.27 g, 1 mmol) was added to a solution of $L^1{\cdot}H_2O$ (0.29 g, 1 mmol) in ethanol (40 cm^3) to give a dark red solution. Glacial acetic acid (0.30 g, 5 mmol) and tri-n-butylamine (0.95 g, 5 mmol) were added with stirring. The solution turned a deep bottle green colour (*ca.* 5 min.) and was filtered. The green microcrystals which deposited overnight were filtered off, washed with ethanol then diethyl ether, and air dried (0.34 g, 75%) (Found: C, 49.10; H, 4.40; Cl, 7.60; N, 15.35. $C_{37}H_{40}Cl_2Fe_2N_{10}O_6$ requires C, 49.20; H, 4.50; Cl, 7.85; N, 15.50%).

$[Fe_2L^1{}_2(\mu\text{-}O)(\mu\text{-}PhCO_2)_2]Cl_{1.5}(PhCO_2)_{0.5}{\cdot}3H_2O{\cdot}EtOH$ (**15**). This was prepared as for (**14**) but using benzoic acid; green microcrystals (0.28 g, 25%). Microanalysis suggested the presence of mixed anions (Found: C, 54.50; H, 5.00; Cl, 4.60, 4.90; N, 11.90. $C_{51.5}H_{54.5}Cl_{1.5}Fe_2N_{10}O_{10}$ requires C, 53.40; H, 4.80; Cl, 4.70; N, 12.30%).

$[Fe_2L^1{}_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2][ClO_4]_2{\cdot}H_2O$ (**16**). Iron(III) perchlorate decahydrate (0.54 g, 1 mmol) was added to a solution of $L^1{\cdot}H_2O$ (0.29 g, 1 mmol) in methanol (40 cm^3) to give a clear, dark red solution. Upon addition of glacial acetic acid (0.30 g, 5 mmol) and 2-methylpyridine (0.47 g, 5 mmol) the colour changed rapidly to a deep green. Diethyl ether was added carefully until the turbidity just redissolved. Upon standing green microcrystals were deposited. These were filtered off, washed with ethanol then diethyl ether, and air dried (0.36 g, 71%) (Found: C, 42.80; H, 3.40; Cl, 7.10; N, 13.45. $C_{36}H_{38}Cl_2Fe_2N_{10}O_{14}$ requires C, 42.80; H, 3.80; Cl, 7.00; N, 13.80%).

$[Fe_2L^1{}_2(\mu\text{-}O)(\mu\text{-}PhCO_2)_2][ClO_4]_2{\cdot}H_2O$ (**17**) This was prepared as for (**16**) but using benzoic acid; green microcrystals (0.41 g, 72%) (Found: C, 48.20; H, 3.70; Cl, 6.50; N, 11.90. $C_{46}H_{42}Cl_2Fe_2N_{10}O_{14}$ requires C, 48.40; H, 3.70; Cl, 6.20; N, 12.30%).

$[Fe_2L^1{}_2(\mu\text{-}O)(\mu\text{-}PhCH_2CO_2)_2][ClO_4]_2{\cdot}2H_2O$ (**19**). This was prepared as for (**17**) but using phenylacetic acid; green microcrystals (0.23 g, 44%) (Found: C, 48.30; H, 4.10; Cl, 6.30; N, 11.70. $C_{48}H_{48}Cl_2Fe_2N_{10}O_{15}$ requires C, 48.55; H, 4.10; Cl, 6.00; N, 11.80%).

$[Fe_2L^1{}_2(\mu\text{-}O)(\mu\text{-}C_{10}H_7CO_2)_2][ClO_4]_2{\cdot}[MeC_5H_4NH][ClO_4]{\cdot}2H_2O$ (**20**). This was prepared as for (**16**) but using naphthalene-2-carboxylic acid; khaki green microcrystals (0.45 g, 62%) (Found: C, 49.20; H, 4.05; Cl, 7.40, 7.60; N, 10.35. $C_{60}H_{56}Cl_3Fe_2N_{11}O_{19}$ requires C, 49.60; H, 3.90; Cl, 7.30; N, 10.60%).

$[Fe_2L^3{}_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2][ClO_4]_2{\cdot}H_2O$ (**21**). Iron(III) chloride tetrahydrate (0.27 g, 1 mmol) and $L^3{\cdot}3H_2O$ (0.33 g, 1 mmol) were allowed to react in ethanol (30 cm^3) to give a yellow–orange suspension of $[FeL^3Cl_3]$. Glacial acetic acid (0.18 g, 3 mmol) and tri-n-butylamine (0.57 g, 3 mmol) were added and the mixture warmed with stirring until a clear, dark green solution was formed (*ca.* 10 min). Addition of saturated ethanolic sodium perchlorate (*ca.* 3 cm^3) resulted in the precipitation of a green powder. The crude product was dissolved in acetonitrile (5 cm^3) and then diluted to 30 cm^3 with ethanol. A small amount of white residue was filtered off and discarded. Addition of saturated ethanolic sodium perchlorate (1 cm^3) induced the deposition of (**21**)$\cdot H_2O$ as green microcrystals. These were filtered off, washed with ethanol, and air dried (0.40 g, 73%) (Found: C, 45.80; H, 4.80; Cl, 6.50; N, 12.60. $C_{42}H_{50}Cl_2Fe_2N_{10}O_{14}$ requires C, 45.80; H, 4.60; Cl, 6.40; N, 12.70%).

$[Fe_2L^3{}_2(\mu\text{-}O)(\mu\text{-}PhCO_2)_2][ClO_4]_2{\cdot}H_2O$ (**22**). This was prepared and recrystallised as for (**21**) but using benzoic acid; green microcrystals (0.35 g, 57%) (Found: C, 50.90; H, 4.70; Cl, 5.60, N, 11.20. $C_{52}H_{54}Cl_2Fe_2N_{10}O_{14}$ requires C, 51.00; H, 4.40; Cl, 5.80; N, 11.40%).

Carboxylate Exchange Reactions of Complex (**22**).—*Method* (*a*). *Preparation of* (**21**)$\cdot H_2O$. A suspension of (**22**)$\cdot H_2O$ (0.50 g, 0.41 mmol) was refluxed with glacial acetic acid (1 cm^3) in ethanol (40 cm^3) for 1 h. The solution was cooled, the green powder filtered off, washed with ethanol then diethyl ether, and air dried (0.39 g, 86%). The i.r. spectrum of the product was identical to that of (**21**).

Method (*b*). *Preparation of* $[Fe_2L^3{}_2(\mu\text{-}O)(\mu\text{-}Me_3CCO_2)_2][ClO_4]_2{\cdot}MeCN$ (**23**). Complex (**22**) (0.50 g, 0.41 mmol) was dissolved in acetonitrile (10 cm^3) with trimethylacetic acid (1.02 g, 10 mmol). Tetra-n-butylammonium perchlorate (1 g) in ethanol (15 cm^3) was added and the solutions filtered. Diethyl ether was added carefully until the turbidity formed just redissolved. Upon standing overnight (**23**)$\cdot$MeCN was deposited as thin, green plates (0.38 g, 77%) (Found: C, 49.90; H, 5.50; Cl, 5.70; N, 13.10. $C_{50}H_{63}Cl_2Fe_2N_{11}O_{13}$ requires C, 49.70; H, 5.25; Cl, 5.90; N, 12.75%).

$[Fe_2L^3{}_2(\mu\text{-}O)(\mu\text{-}HOC_6H_4CO_2)_2][ClO_4]_2{\cdot}2H_2O$ (**24**). This was prepared as for (**23**) but using 4-hydroxybenzoic acid; green, feathery microcrystals (0.48 g, 92%) (Found: C, 49.30; H, 4.20; Cl, 5.70; N, 10.80. $C_{52}H_{56}Cl_2Fe_2N_{10}O_{17}$ requires C, 49.00; H, 4.40; Cl, 5.60; N, 11.00%).

$[Fe_2L^3{}_2(\mu\text{-}O)(\mu\text{-}MeCONHC_6H_4CO_2)_2][ClO_4]_2{\cdot}2H_2O$ (**25**). This was prepared as for (**23**) but using 4-acetamidobenzoic acid; rosettes of very thin, green needles (0.43 g, 77%) (Found: C, 49.90; H, 4.40; Cl, 5.30; N, 12.15. $C_{56}H_{62}Cl_2Fe_2N_{12}O_{17}$ requires C, 49.50; H, 4.60; Cl, 5.20; N, 12.40%).

Results and Discussion

Tricarbonylmolybdenum(0) *Complexes of the Tripodal Ligands* L^1—L^3.—Many nitrogen containing ligands form octahedral molybdenum(0) complexes of general formula $[MoL(CO)_3]$,[5] where L represents one or more ligands providing three nitrogen donor atoms. Uusually the nitrogen ligand(s) co-ordinate in a facial manner, but meridional co-ordination is observed when steric effects dominate. The two geometries are

Table 1. I.r. spectral data[a] for $[MoL(CO)_3]$ complexes

Complex	ν_1	ν_2	ν_3
(4) *fac*-$[Mo(dien)(CO)_3]$[b]	1 887[c]	1 734	
(5) *fac*-$[Mo(CO)_3(MeCN)_3]$	1 915[c]	1 783	
(6) *fac*-$[Mo(tacn)(CO)_3]$[d]	1 850[e]	1 720 (br)	
(7) *mer*-$[Mo(CN)_3(CO)_3]$	1 975[c]	1 900	1 832

[a] In cm^{-1}. [b] dien = diethylenetriamine. [c] As Nujol mull. [d] tacn = 1,4,7-triazacyclononane. [e] As KBr pellet.

Table 2. I.r.[a] and positive ion f.a.b. mass spectral data for complexes (1)—(3)

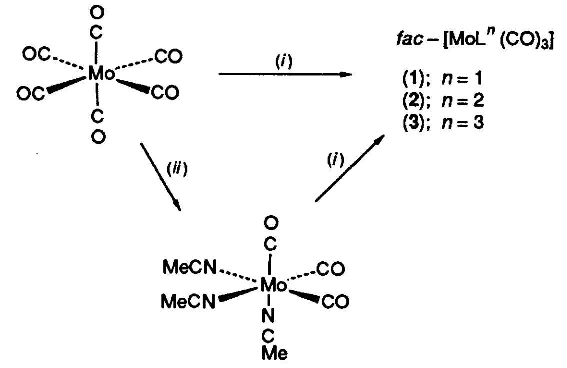
Complex	ν_1	$\nu_2(1)$	$\nu_2(2)$	M^+ (%)
(1) $[MoL^1(CO)_3]$	1 884	1 761	1 723	—
(2) $[MoL^2(CO)_3]$	1 891	1 771	1 702	473[b] (100)
(3) $[MoL^3(CO)_3]$	1 890	1 763	1 748	501[c] (100)

[a] In cm^{-1} (KBr disc). [b] For ^{98}Mo (noba matrix). [c] For ^{98}Mo (sulpholane matrix).

distinguished by characteristic i.r. bands in the carbonyl region (Table 1).[6]

The molecular structure of (4) has been determined by *X*-ray crystallography and confirms the facial co-ordination of the carbonyls.[7] With the three *fac* complexes (4)—(6) ν_2 is more intense than ν_1, and usually broadened due to partial lifting of the degeneracy of its two components. The *mer* complex (7) gives three strong bands with a significant shift to higher energy. With the flexible, tridentate ligands mentioned above only *fac*-$[MoL(CO)_3]$ complexes have been identified. Thus L^1—L^3 should co-ordinate the $Mo(CO)_3$ fragment in the preferred facial manner. These ligands also co-ordinate facially in some complexes of iron and manganese[2] and such compounds have been prepared in order to allow a comparison of their i.r. spectra, enabling bands associated with the facially co-ordinated ligand to be identified. This was essential to allow the assignment of other bands of interest in the model compounds. The $Mo(CO)_3$ complexes of the tridentate ligands L^1—L^3 were prepared in one of two ways; either by direct reaction of the ligands with $[Mo(CO)_6]$ in refluxing acetonitrile [Method (*a*)], or by substitution of the labile acetonitrile ligands in $[Mo(CO)_3(MeCN)_3]$[Method (*b*)] (Scheme 1).

The complexes (1)—(3) were obtained directly from the reaction mixtures as air-stable, pale yellow powders or microcrystalline solids. All three are completely insoluble in common organic solvents. Positive ion f.a.b. mass spectrometry gives poor quality spectra (Table 2). No spectrum is observed for (1), but molecular ions are assignable for (2) and (3), and have approximately the correct isotopic pattern for molybdenum. Use of e.i. and c.i. (ammonia) mass spectrometry only gave spectra with peaks corresponding to ligand fragments. The i.r. spectra in the carbonyl region show bands consistent with facial co-ordination of the ligands.



Scheme 1. (*i*) L^n, MeCN, reflux, N_2; (*ii*) MeCN, reflux, N_2

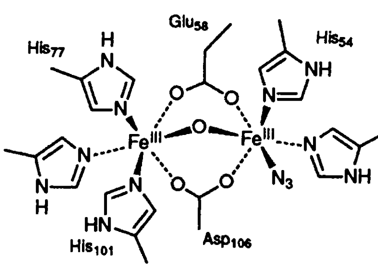


Figure 1. Azidomethaemerythrin

In all these complexes the symmetry of the first co-ordination sphere of the molybdenum atom is approximately C_{3v}, giving rise to two vibrational modes ν_1 (*a'*) and ν_2 (*e*), the second of which comprises two degenerate components. With L^1 and its derivatives however the nitrogen donor atoms are of two distinct types and therefore the corresponding *fac*-$[MoL^n(CO)_3]$ complexes are of lower overall symmetry. With the ligand bound symmetrically the point group is now C_s and the degeneracy of the ν_2 (*e*) mode has been lifted, giving altogether three distinct modes ν_1 (*a'*), $\nu_2(1)$ (*a''*), and $\nu_2(2)$ (*a''*). For $[Mo(CO)_3(MeCN)_3]$ (5) only a single, broad band is still observed for $\nu_2(1)$ and $\nu_2(2)$.[8] For (3) however, the two bands overlap significantly; the maxima are distinguishable (Δ = 15 cm^{-1}). Much greater splittings of 38 and 69 cm^{-1} are observed for (1) and (2) respectively. It is reasonable to assume that the geometries of all three complexes are very similar, yet the relative positions of the $\nu_2(1)$ and $\nu_2(2)$ bands differ greatly. Notably the replacement of the acidic N–H groups of the benzimidazoles in (2) with N–Me groups will have an insignificant steric effect, indicating that intermolecular hydrogen bonding is an important factor influencing the band positions of (1) and (2).

Dinuclear Iron(III) *Complexes of* L^1 *and* L^3 *containing the* $[Fe_2(\mu\text{-}O)(\mu\text{-}RCO_2)_2]^{2+}$ *Core*.—Both the met- and azidomet-forms of haemerythrin[9] have been characterised by *X*-ray crystallography to a resolution of 2.0 Å, and have been shown to contain the $[Fe_2(\mu\text{-}O)(\mu\text{-}RCO_2)_2]^{2+}$ triply bridged core. Similar di-iron cores are thought to be present in ribonucleotide reductase, methane mono-oxygenase, and some purple acid phosphatases. In azidomethaemerythrin both iron atoms are six-co-ordinate with an N_3O_3 donor set, the three nitrogen donor atoms on each iron atom being bound in an approximately facial orientation (Figure 1).

Azidomethaemerythrin is an obvious candidate for modelling studies as superficially the two iron atoms are in identical, octahedral environments. The use of facially co-ordinating tridentate nitrogen donor ligands allows the formation of the desired symmetrical dinuclear iron(III) complexes by spontaneous self assembly. The model compounds (8),[10] (9),[11] (10),[12] and (11)[13] have been prepared using the ligands 1,4,7-triazacyclononane, its tris-*N*-methyl derivative, the hydrotris(1-pyrazolyl)borate anion, and *N,N,N',N'*-tetra(2-pyridylmethyl)-1,4-diaminobutane respectively. The bidentate nitrogen donor ligand 2,2'-bipyridyl has also been used to prepare the analogous complexes (12)[14] and (13)[14] with a terminal anionic ligand (Cl^- or N_3^-) bound to each iron (Figure 2). These systems are of specific relevance as corroborative models for met-, chloromet-, and azidomethaemerythrin as the iron environments are approximately reproduced, but are also of value for understanding the other

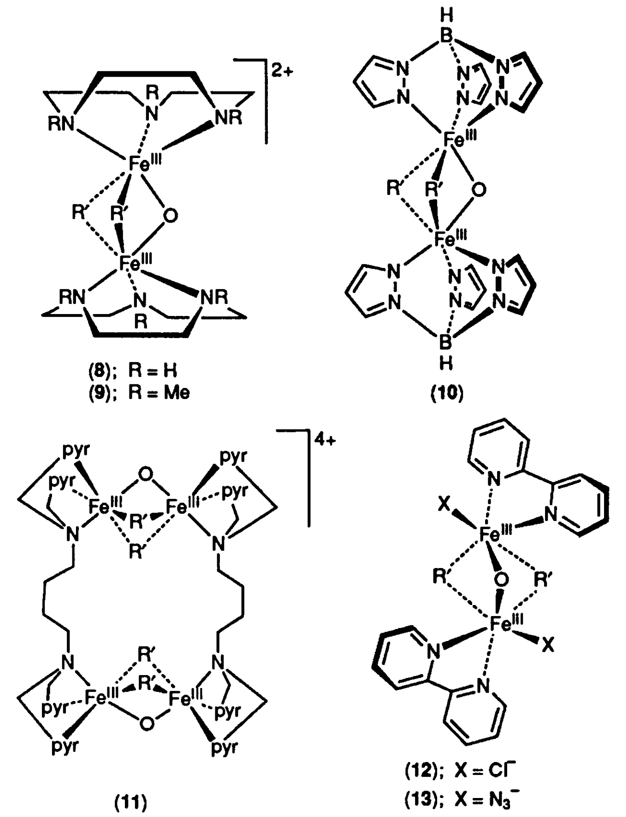
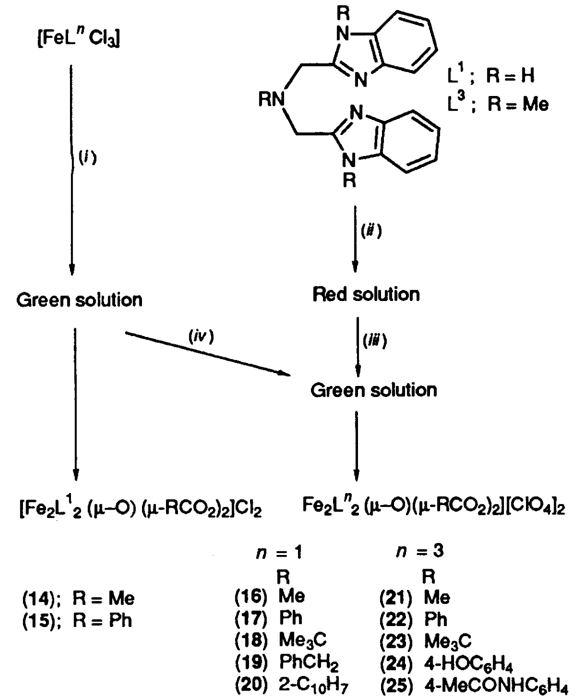


Figure 2. Models for azidomethaemerythrin; pyr = $-C_5H_4N$ and R′ = $MeCO_2$



Scheme 2. (*i*), $n = 1$ or 3, ROH-RCO_2H, base; (*ii*) ROH, $Fe(ClO_4)_3{\cdot}10H_2O$; (*iii*) RCO_2H, base; (*iv*) $NaClO_4$, $n = 1$, R = Me_3C; $n = 3$, R = all

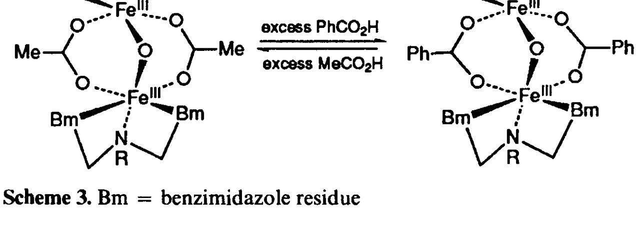
metalloproteins as they contain the $[Fe_2(\mu\text{-}O)(\mu\text{-}RCO_2)_2]^{2+}$ core.

The flexible, tridentate ligand L^1 and its tris-*N*-methyl derivative L^3 contain imidazole moieties and should form dinuclear iron(III) complexes analogous to those described above. Indeed the assembly of the $[Fe_2(\mu\text{-}O)(\mu\text{-}RCO_2)_2]^{2+}$ core in the presence of L^1 occurs spontaneously. The reaction of L^1 and iron(III) chloride with an excess of carboxylate in alcoholic solution gave a clear, dark green solution, from which the chloride salts of the triply bridged dinuclear iron(III) complexes were deposited as green microcrystals. The analysis of the benzoate complex consistently indicated the presence of mixed anions, $3Cl^-:1PhCO_2^-$. Identical products were obtained by treating a suspension of $[FeL^1Cl_3]$ with an excess of carboxylate. It is interesting that during the course of this second reaction the ligand is required to switch from a meridional to a facial mode of co-ordination.

These chloride salts have poor solubilities so the corresponding compounds with perchlorate as the counter ion were prepared. For the trimethylacetic acid derivative the chloride salt did not crystallise out but addition of an excess of sodium perchlorate enabled isolation of the desired product. The remaining complexes were prepared by using iron(III) perchlorate directly (Scheme 2). The crystal structure of (**18**) has been solved and verifies the presence of the $[Fe_2(\mu\text{-}O)(\mu\text{-}RCO_2)_2]^{2+}$ core[2] as does the structure of the homologous complex $[Fe_2L^1{}_2(\mu\text{-}O)(\mu\text{-}PhCO_2)_2][ClO_4]_2$ (**26**).[15] *N,N*-Bis(*N*′-alkylbenzimidazol-2-ylmethyl)amine (L′) complexes of the type $[Fe_2L'_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2][ClO_4]_2$ have recently been reported where the *N*′-alkyl group is ethyl, propyl, butyl, or benzyl.[16]

Analogous reactions were carried out with the ligand L^3. With this system the chloride salts did not crystallise out of alcoholic solution, but addition of an excess of sodium perchlorate enabled the species $[Fe_2L^3{}_2(\mu\text{-}O)(\mu\text{-}RCO_2)_2][ClO_4]_2$ to be isolated. The perchlorate salts of the complexes of L^1 were all isolated as pure, green [with the exception of (**20**)], microcrystalline solids directly from the reaction mixture. The naphthalene-2-carboxylic acid complex (**20**) was isolated as khaki green microcrystals, the elemental analysis of which indicated that it was a mixed salt with one equivalent of 2-methylpyridinium perchlorate per dinuclear iron unit. (2-Methylpyridine was the base used to deprotonate the naphthalene-2-carboxylic acid *in situ*.) This was confirmed from the ^1H n.m.r. spectrum of (**20**) in $(CD_3)_2CO$. All the signals for the complex were broadened due to the paramagnetic iron centres but sharp signals corresponding to solvent impurities and the free 2-methylpyridinium cation [δ_H 8.90 (1 H, m), 8.65 (1 H, m), 8.10 (2 H, m), and 2.94 (3 H, s)] were assignable.

The complexes of L^3 were initially isolated as impure, green powders. These were recrystallised by dissolving in the minimum volume of acetonitrile, diluting the solution with ethanol, followed by addition of the appropriate amount of saturated, ethanolic sodium perchlorate. The complexes were all obtained as green microcrystals. Recrystallisation in the presence of an excess of a different carboxylic acid resulted in carboxylate exchange. Excluding experimental losses the exchange was quantitative and was used to prepare other derivatives of $[Fe_2L^3{}_2(\mu\text{-}O)(\mu\text{-}RCO_2)_2][ClO_4]_2$ (Scheme 3).



Scheme 3. Bm = benzimidazole residue

Table 3. Positive ion f.a.b. mass spectra assignments for $[Fe_2L^n{}_2(\mu\text{-}O)(\mu\text{-}RCO_2)_2][ClO_4]_2$ derivatives (n = 1 or 3)[a,b]

Fragment	**(16)**	**(17)**	**(18)**	**(19)**	**(20)**
$[Fe_2L^1{}_2O(RCO_2)_2(ClO_4)]^+$	899 (5)	1 023 (26)	983 (11)	1 051 (5)	1 123 (5)
$[Fe_2L^1{}_2O(RCO_2)(ClO_4)-H]^+$	839 (8)	901 (50)	881 (5)	915 (11)	951 (17)
$[Fe_2L^1{}_2O(RCO_2)-2H]^+$	739 (10)	801 (92)	781 (23)	815 (26)	851 (15)
$[FeL^1(RCO_2)]^+$	392 (30)	454 (33)	434 (100)	468 (55)	504 (59)
	(21)	**(22)**	**(23)**	**(24)**	**(25)**
$[Fe_2L^3{}_2O(RCO_2)_2(ClO_4)]^+$	983 (15)	1 107 (22)	1 067 (11)	1 139 (12)	1 221 (11)
$[Fe_2L^3{}_2O(RCO_2)_2]^+$	*c*	1 008 (5)	963 (3)	1 040 (4)	1 122 (11)
$[Fe_2L^3{}_2O(RCO_2)(ClO_4)]^+$	*c*	986 (3)	*c*	1 002 (2)	*c*
$[Fe_2L^3O(RCO_2)_2(ClO_4)]^+$	*c*	788 (33)	748 (52)	820 (15)	902 (12)
$[Fe_2L^3O(RCO_2)_2]^+$	*c*	689 (21)	649 (24)	721 (14)	803 (12)
$[FeL^3(RCO_2)]^+$	434 (100)	496 (100)	476 (90)	512 (100)	553 (95)

[a] Numbers in parentheses are relative % intensity. [b] noba Matrix, peaks corresponding to ^{56}Fe and ^{35}Cl isotopes. [c] No peak apparent over background noise.

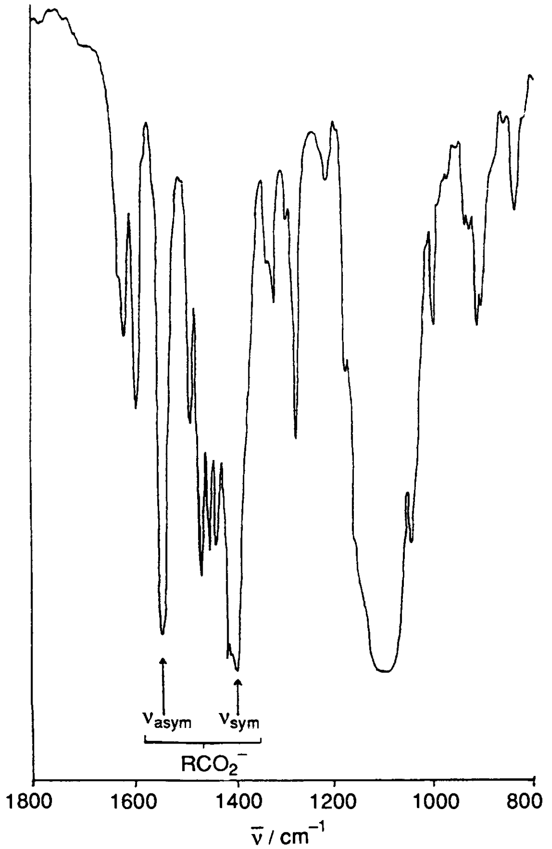


Figure 3. I.r. spectrum of complex (**17**) in the region 1 800—800 cm^{-1}

This reaction worked equally well for the derivatives of L^1 and apparently for the $[Fe_2(\mu\text{-}O)(\mu\text{-}RCO_2)_2]^{2+}$ core in general.[17] It has been observed that acidic conditions are essential, indicating that the protonation of one of the bridging groups is a necessary first step in the exchange mechanism.

The chloride salts (**14**) and (**15**) do not give readily interpretable positive ion f.a.b. mass spectra, presumably due to their insolubility. Only low-mass peaks corresponding to mononuclear fragments are observed. The more soluble perchlorate salts however give clean spectra in which bridged dinuclear iron(III) species are assignable (Table 3). In the spectra of all 10 derivatives the highest mass peak observed corresponds to $[Fe_2L_2O(RCO_2)_2(ClO_4)]^+$, however the complexes of L^1 and L^3 fragment differently. For the derivatives of L^1 peaks for $[Fe_2L^1{}_2O(RCO_2)(ClO_4)-H]^+$ and $[Fe_2L^1{}_2O(RCO_2)-2H]^+$ are observed but those of $[Fe_2L^1O(RCO_2)_2-H]^+$ are not. The missing protons are probably lost from the acidic benzimidazole N–H groups. Similar peaks are observed for the L^3 derivatives but without this proton loss. More dinuclear iron fragments are observed for the L^3 complexes. In the spectra of four of the complexes weak $[Fe_2L^3{}_2O(RCO_2)_2]^+$ peaks are now apparent. Surprisingly loss of one ligand from the dinuclear iron unit is also observed, giving medium intensity peaks corresponding to $[Fe_2L^3O(RCO_2)_2(ClO_4)]^+$ and $[Fe_2L^3O(RCO_2)_2]^+$.

In the i.r. spectra of these complexes the antisymmetric and symmetric stretching modes of the carboxylate groups are assigned readily. The spectrum of (**17**) in the 1 800—800 cm^{-1} region is typical (Figure 3). For the range of derivatives the exact position of these bands vary slightly due to the nature of the R group of the carboxylic acid, and are broadly comparable to the values found for other azidomethaemerythrin models (Table 4). The assignments of the Fe–O(oxo)–Fe′ antisymmetric and symmetric stretching modes are less straightforward due to the large number of bands in the 800—450 cm^{-1} region. For the complexes of L^1 comparison with the spectrum of *fac*-$[MoL^1(CO)_3]$ (**1**) allows many of these bands to be identified as ligand based modes (Figure 4). This enables the assignment of the symmetric modes at around 535 cm^{-1}. Unfortunately the antisymmetric modes overlap significantly and can only be assigned around 730 cm^{-1} in favourable cases. In the benzoate complexes the out of plane C–H bending mode of the phenyl ring occurs at *ca.* 735 cm^{-1} and completely obscures the antisymmetric Fe–O(oxo)–Fe′ stretch. By the same strategy these modes for the complexes of L^3 can be assigned by comparison with $[MoL^3(CO)_3]$ (**3**). There are a few minor differences between the L^3 and L^1 derivatives, the only consistent one being a tendency for the symmetric Fe–O(oxo)–Fe′ stretch to occur at slightly lower energy. These values are typical for dinuclear iron(III) complexes of this type but differ from the reported values of 507 and 770 cm^{-1} for azidomethaemerythrin, and 492 and 796 cm^{-1} for ribonucleotide reductase.[1,9] The assignments of both modes for all the derivatives are summarised in Table 4.

A recent survey of the electronic and Raman spectroscopic properties of oxo-bridged dinuclear iron centres in proteins and model complexes offers the generalisation that the electronic spectra include two very intense bands in the near-u.v. (320—380 nm) and several less intense bands in the visible region (430—550 nm).[18] The former are assigned to oxo $\longrightarrow$ iron charge-transfer bands and the latter are due to ligand-field transitions. Electronic absorption spectra of the chloride salts

Table 4. Comparison of the ν_{asym} and ν_{sym} carboxylate and Fe–O–Fe′ modes of $[FeL^{n}{}_2(\mu\text{-}O)(\mu\text{-}RCO_2)_2]^{2+}$ with azidomethaemerythrin, ribonucleotide reductase, and other model compounds[a]

Complex	R	$\nu_{asym}(RCO_2)$	$\nu_{sym}(RCO_2)$	ν_{asym}(Fe–O–Fe)	ν_{sym}(Fe–O–Fe)
(14)	Me	1 566	1 440[b]	720	532
(15)	Ph	1 545	1 440	*c*	537
(16)	Me	1 561	1 440[b]	730[d]	539
(17)	Ph	1 546	1 400	*c*	538
(18)	Me_3C	1 550	1 423[b]	724	549
(19)	$PhCH_2$	1 561	1 397	*c*	541
(20)	$2\text{-}C_{10}H_7$	1 550	1 400	726	540
(21)	Me	1 560	1 445[b]	724	535
(22)	Ph	1 540	1 400	*c*	535
(23)	Me_3C	1 545	1 420[b]	729	534
(24)	$4\text{-}HOC_6H_4$	1 505[b]	1 390	730[d]	534
(25)	$4\text{-}MeCONHC_6H_4$	1 505[b]	1 390	730[d]	534
Azidomethaemerythrin[1]	$R'CH_2$			770	507
Ribonucleotide reductase[1]	$R''CH_2$			756	492
(8)[10]	Me			730	
(9)[11]	Me	1 540	1 442	710	
(10)[12]	Me	1 560	1 427	751	528
(11)[13]	Me	1 500	1 440	725	

[a] In cm^{-1} (KBr disc). [b] Overlapping with ligand bands. [c] Obscured by phenyl band at 725 cm^{-1} (see text). [d] Shoulder.

Table 5. Electronic absorption spectral data[a] for $[Fe_2L^{n}{}_2(\mu\text{-}O)(\mu\text{-}RCO_2)_2]^{2+}$ ($n = 1$ or 3) compared to other model compounds and azidomethaemerythrin

(*i*) Derivatives of $[Fe_2L^1{}_2(\mu\text{-}O)(\mu\text{-}RCO_2)_2][ClO_4]_2$				
(16)	**(17)**	**(18)**	**(19)**	**(20)**
354 (3 886)	356 (3 037)	356 (4 054)	357 (3 562)	358[b] (5 026)
479[b] (279)	481[b] (192)	481[b] (254)	481[b] (244)	480[b] (237)
489 (287)	488 (198)	488 (257)	489 (251)	488 (244)
523[b] (101)	521 (68)	522 (103)	520 (84)	521 (84)
625 (74)	606 (60)	600 (87)	614 (66)	605 (75)
(*ii*) Derivatives of $[Fe_2L^3(\mu\text{-}O)(\mu\text{-}RCO_2)_2][ClO_4]_2$				
(21)	**(22)**	**(23)**	**(24)**	**(25)**
364 (4 594)	369 (4 675)	368 (4 919)	358 (5 609)	359 (6 661)
483[b] (269)	483[b] (264)	481[b] (271)	481[b] (264)	481[b] (278)
492 (285)	493 (276)	493 (281)	492 (273)	492 (285)
525 (99)	528 (95)	530 (108)	528 (104)	527 (105)
609 (82)	610 (89)	610 (106)	608 (91)	608 (96)
(*iii*) Other model compounds and azidomethaemerythrin				
(8)[10]	**(10)**[12]	**(11)**[13]	**(26)**[15]	Azidomethaemerythrin[1]
335 (1 840)	339 (4 635)	348 (3 678)	355 (4 000)	326[b] (3 375)
464 (269)	457 (506)	470 (554)	485 (310)	446 (1 850)
506 (199)	492 (406)	505 (493)	525 (110)	
543[b]	528[b]		560[b]	
743 (33)	695 (70)	730 (79)	620 (50)	680 (95)

[a] $\lambda_{max.}$ nm (ε $dm^3\,mol^{-1}\,cm^{-1}$ per Fe). [b] Shoulder.

(14) and **(15)** in solution could not be recorded due to their insolubility. The perchlorate salts however, are moderately soluble in acetonitrile and give deep green solutions. The spectra in the range 300—900 nm of all ten compounds have the same basic form, with no significant difference between the complexes of L^1 and L^3. A broad envelope is observed around 355—360 nm and this is comparable to that reported for other azidomethaemerythrin models and for azidomethaemerythrin itself.[19,20] Only for **(20)** (329 nm) and **(22)** (323 nm) are the shoulders detected that have been reported for some model compounds derived from the hydridotris(1-pyrazoyl)borate anion and the 1,4,7-triazacyclononane macrocycles.[19,21] The spectra of the remaining complexes are directly comparable with that reported for the homologous complex **(26)**.[15] Ligand-field transitions are noted in the region 400—650 nm. Details of all 10 spectra, and a comparison with other models and azidomethaemerythrin are given in Table 5.

The greater solubility of the complexes of L^3 in acetonitrile allows their investigation by ^1H n.m.r. spectroscopy. The acetate **(21)** and trimethylacetate **(23)** complexes were studied to enable the assignment of the carboxylate CH_3 protons. These complexes are paramagnetic but the strong antiferromagnetic coupling results in the whole spectrum occurring in the range δ 0.0—20.0. Only signals for the dinuclear iron(III) moiety are

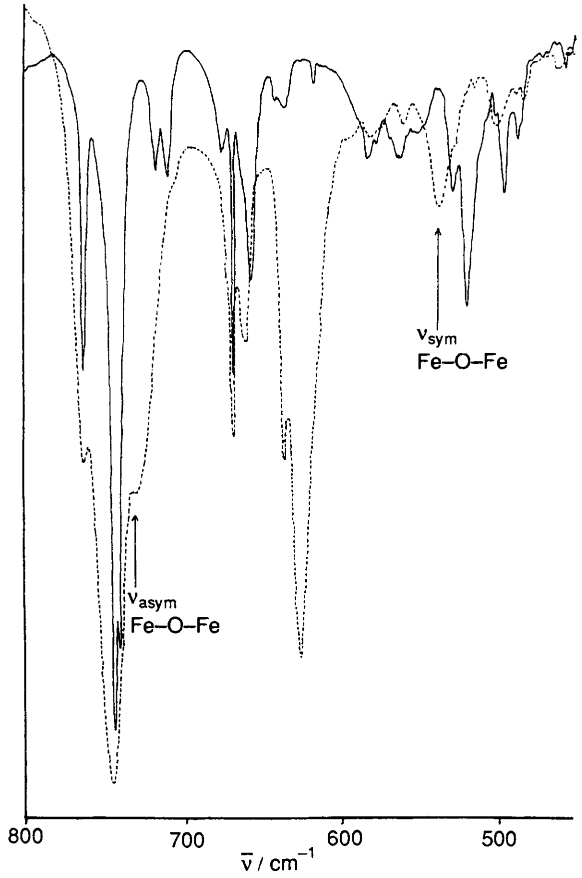


Figure 4. Assignment of the antisymmetric and symmetric Fe–O–Fe′ stretching modes of complex (**16**) (– – – –) by comparison with *fac*-[MoL^1(CO)$_3$] (**1**) (——)

Table 6. ^{1}H N.m.r. assignments of the carboxylate methyl resonances of complexes (**21**) and (**23**) in acetonitrile.

Complex	δ(co-ordinated)	δ(free acid)	Δδ
(**21**)	9.20	2.06^a	7.14
(**23**)	2.60	1.21^b	1.39

^{a} CCl_4 Solution. ^{b} $CDCl_3$ Solution.

broadened, those for $SiMe_4$ and solvent impurities being sharp. Most of the ligand signals cannot be assigned on the basis of these two spectra but the *N*-methyl groups of the benzimidazoles are tentatively assigned to the strong resonance at δ 5.60. The $-CH_3$ protons of the bridging acetates in (**21**) appear as a broad resonance at δ 9.20. This signal does not appear for complex (**23**) but is replaced by a stronger resonance at δ 2.60 due to the $-C(CH_3)_3$ group of the bridging trimethylacetate groups. The protons of the tertiary butyl group are further from the paramagnetic centres hence this resonance is sharper and appears closer to the value for the free carboxylic acid than does the acetate resonance (Table 6). The position of the acetate signal in (**21**) is comparable to that observed for the azidomethaemerythrin model compound (**10**) (δ 10.5).[19]

Acknowledgements

We thank the S.E.R.C. for a support grant.

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Received 29*th May* 1990; *Paper* 0/02377I