New Triply Bridged Diiron(III) Complexes with $[Fe_2(\mu\text{-}O)(\mu\text{-}X)_2]^{2+}$ Cores [X = $MeCO_2$, $PhCO_2$ or $(PhO)_2PO_2$]

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A group of three diiron(III) complexes having $[Fe_2(\mu\text{-}O)(\mu\text{-}X)_2]^{2+}$ cores (X = benzoate, acetate or diphenyl phosphate) has been synthesised with the use of unsymmetrical facially capping tridentate ligands (L^1 and L^2), where L^1 and L^2 are [2-(2-pyridyl)ethyl](2-pyridylmethyl)amine and methyl[2-(2-pyridyl)ethyl](2-pyridylmethyl)amine respectively. The lability of the bridging acetate groups in $[Fe(\mu\text{-}O)(\mu\text{-}MeCO_2)_2L^2_2]^{2+}$ has been demonstrated by exchange with diphenyl phosphate and deuterioacetate as revealed by UV/VIS and ^1H NMR studies. These complexes exhibit infrared, electronic and Mössbauer spectral features very similar to those of μ-oxo-diiron(III) proteins as well as of μ-oxo-bis(μ-carboxylato) or μ-oxo-bis(μ-phosphato)diiron(III) complexes. The inequivalence in the chelate rings around each iron(III) might have caused the asymmetry in these compounds which is reflected in their distinctively strong antiferromagnetic coupling ($J = -127$, -125 and $-108\ cm^{-1}$ for the benzoate-, acetate- and phosphate-bridged complexes respectively).

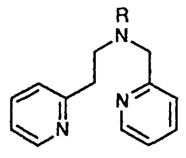
Haemerythrin,[1] a marine invertebrate respiratory protein, is prototypical of an emerging class of oxo-bridged non-haem iron proteins and enzymes,[1-3] including ribonucleotide reductase, purple acid phosphatases, methane monooxygenase and rubrerythrin. To understand the chemistry of the assembly and function of these metalloproteins a large number of tri-bridged[4-11] models have been synthesised by using a variety of tridentate N-based ligands.

The present work stems from our continued interest[12] in the synthesis and reactivity of dimetal complexes having $(\mu\text{-}O)(\mu\text{-}MeCO_2)_2$ triply bridged cores. Herein we report the syntheses of a group of three triply bridged diiron(III) complexes with $[Fe_2(\mu\text{-}O)(\mu\text{-}X)_2]^{2+}$ cores [X = $MeCO_2$, $PhCO_2$ or $(PhO)_2PO_2$] using facially capping tridentate amine ligands (L^1 and L^2). These new complexes have been characterized by elemental analyses, solution electrical conductivity, spectral (IR, UV/VIS, Mössbauer and ^1H NMR) and magnetic susceptibility measurements. We also report the results of acetate bridge-exchange reactions of $[Fe_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2L^2_2]^{2+}$ (*i*) with CD_3CO_2D producing $[Fe_2(\mu\text{-}O)(\mu\text{-}CD_3CO_2)_2L^2_2]^{2+}$ and (*ii*) with $(PhO)_2PO_2H$ producing $[Fe_2(\mu\text{-}O)\{\mu\text{-}(PhO)_2PO_2\}_2L^2_2]^{2+}$.

Experimental

Chemicals and Starting Materials.—Solvents and reagents were obtained from commercial sources and used without further purification unless otherwise stated. Acetonitrile and diethyl ether were dried/purified as described previously.[13-15] The compound $[NEt_4]_2[Fe_2OCl_6]$ was prepared following a literature method.[16]

Preparation of Ligands.—The ligands [2-(2-pyridyl)ethyl](2-pyridylmethyl)amine (L^1) and methyl[2-(2-pyridyl)ethyl](2-pyridylmethyl)amine (L^2) were prepared according to literature procedures.[12,17]



L^1 R = H
L^2 R = Me

Syntheses of Complexes.—$[Fe_2(\mu\text{-}O)(\mu\text{-}PhCO_2)_2L^1_2][ClO_4]_2\cdot 2H_2O$ **1**. A mixture of $[NEt_4]_2[Fe_2OCl_6]$ (820 mg, 1.36 mmol) and $Na(O_2CPh)$ (420 mg, 2.92 mmol) in MeCN (20 cm^3) was stirred for 20 min. The ligand L^1 (600 mg, 2.8 mmol) in MeCN (10 cm^3) was then added slowly over a period of 10 min. The mixture was stirred at 298 K for 4 h. Then solid $NaClO_4\cdot H_2O$ (600 mg, 4.3 mmol) was added. The mixture was stirred for 15 min, filtered and the solvent removed using a rotary evaporator at *ca.* 30–40 °C. The residue was then dissolved in MeCN (10 cm^3) and filtered through a G-4 frit. The brown crystals obtained after cooling (*ca.* 273 K) the filtrate were collected and recrystallized from $MeCN-Et_2O$ (1 : 1 v/v) (yield *ca.* 40%) (Found: C, 46.30; H, 4.30; N, 8.10. Calc. for $C_{40}H_{44}Cl_2Fe_2N_6O_{15}$: C, 46.60; H, 4.30; N, 8.20%). UV/VIS (MeCN), λ/nm ($\varepsilon_{Fe}/dm^3\ mol^{-1}\ cm^{-1}$): 733 (75), 546(sh) (120), 505 (520), 470 (580), 420(sh) (520), 372(sh) (2550), 337 (3950) and 238 (21 350). Λ_M (298 K, MeCN) = 286 $\Omega^{-1}\ cm^2\ mol^{-1}$. IR (KBr, cm^{-1}): ν_{asym}(Fe–O–Fe) 725m; $\nu_{asym}(PhCO_2)$ 1540s; $\nu_{sym}(PhCO_2)$ 1400s; $\nu(ClO_4^-)$ 1090vs; ν(NH) 3260(br) and ν(OH) 3400(br).

$[Fe_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2L^2_2][ClO_4]_2\cdot 2H_2O$ **2**. This complex was synthesised using the ligand L^2 following a similar procedure to that described above, except that $Na(O_2CMe)$ was used (yield *ca.* 55%) (Found: C, 40.95; H, 4.70; N, 9.00. Calc. for $C_{32}H_{44}Cl_2Fe_2N_6O_{15}$: C, 41.10; H, 4.75; N, 9.00%). UV/VIS (MeCN), λ/nm ($\varepsilon_{Fe}/dm^3\ mol^{-1}\ cm^{-1}$): 727 (76), 551(sh) (125), 506 (525), 472 (590), 420(sh) (810), 380(sh) (3000), 347 (3680) and 238 (11 200). Λ_M (298 K, MeCN) = 292 $\Omega^{-1}\ cm^2\ mol^{-1}$. IR (KBr, cm^{-1}): ν_{asym}(Fe–O–Fe) 730m; $\nu_{asym}(MeCO_2)$ 1550s; $\nu_{sym}(MeCO_2)$ 1440s; $\nu(ClO_4^-)$ 1090vs and ν(OH) 3400(br).

$[Fe_2(\mu\text{-}O)\{\mu\text{-}(PhO)_2PO_2\}_2L^2_2][ClO_4]_2\cdot H_2O$ **3**. A mixture of $(PhO)_2PO_2H$ (166 mg, 0.66 mmol) and NEt_3 (67 mg, 0.66 mmol) in MeCN (10 cm^3) was added to a stirred MeCN (10 cm^3) solution of $[NEt_4]_2[Fe_2OCl_6]$ (200 mg, 0.33 mmol). After stirring the mixture for 15 min the ligand L^2 (150 mg, 0.66 mmol) in MeCN (10 cm^3) was added slowly over a period of 10 min. The mixture was stirred at 298 K for 4 h. Then solid $NaClO_4\cdot H_2O$ (300 mg, 2.1 mmol) was added. The mixture was stirred for 15 min, filtered and the solvent removed using a rotary evaporator. The residue was then dissolved in MeCN (10 cm^3) and filtered through a G-4 frit; Et_2O (10 cm^3) was added slowly. Storage of this solution at *ca.* 273 K for 24 h resulted in a green microcrystalline solid. The compound was recrystallized from MeCN–Et_2O (1 : 1 v/v) and dried *in vacuo* (yield *ca.* 50%) (Found: C, 48.30; H, 4.40; N, 6.45. Calc. for $C_{52}H_{56}Cl_2Fe_2N_6O_{18}P_2$: C, 48.10; H, 4.35; N, 6.50%). UV/VIS (MeCN), λ/nm (ε_{Fe}/dm^3 mol^{-1} cm^{-1}): 661 (65), 527(sh) (90), 490(sh) (290), 453(sh) (390), 416(sh) (670), 365(sh) (2900), 329 (4020) and 254 (9600). Λ_M (298 K, MeCN) = 280 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): ν_{asym}(Fe–O–Fe) 735m; $\nu(ClO_4^-)$ + ν(PO) 1195s, 1160m, 1080vs, 1025m and ν(OH) 3400(br).

Measurements.—Infrared spectra were recorded as KBr pellets on a Perkin Elmer FT IR model 1600 instrument, electronic spectra with a Perkin Elmer Lambda 2 spectrophotometer. Solution electrical conductivity was measured on acetonitrile solutions with a type CM-82 T Elico conductivity bridge (Hyderabad, India) and a solute concentration of $\approx 10^{-3}$ mol dm^{-3}. Solution magnetic susceptibility was determined by the conventional NMR method[18] in acetonitrile with a PMX-60 JEOL (60 MHz) NMR spectrometer. Solvent susceptibility[19a] and diamagnetic corrections[19b] were taken from published data. The ^1H NMR spectrum was measured in CD_3CN on a Brüker WM-400 (400 MHz) spectrometer.

For ^{57}Fe Mössbauer spectroscopy, γ-ray resonance spectra were obtained at the Low-temperature Physics Group, Tata Institute of Fundamental Research (TIFR), Bombay, India by using a standard, constant-acceleration spectrometer calibrated with metallic iron at room temperature. All isomer shifts are reported with respect to the room-temperature iron(0) transmission spectrum. The observed spectra were computer-fitted using Lorentzian lines and a least-squares minimization technique.

Variable-temperature magnetic susceptibility measurements were made on powdered samples over the temperature range $8.0 < T < 300$ K by the Faraday method using a locally built susceptometer at the Chemical Physics Group, TIFR, Bombay, India. The measurements were started at ≈ 8.0 K and the sample was heated and held at the desired temperature during the measurement. This process was continued until the sample was again at room temperature. A total of 20–25 data points was taken over the temperature range. Each data point was the mean of three measurements. Effective magnetic moments per Fe^{III} were calculated using the formula $\mu_{eff}^2 = (7.998/2)\chi_M T$, where χ_M is the corrected molar susceptibility. The susceptibility of the sample holder was measured at the same temperature points and subtracted from the observed susceptibility with sample present. The diamagnetic contributions were calculated by using values[19b] of -435×10^{-6} cm^3 mol^{-1} for complex **1**, -387×10^{-6} cm^3 mol^{-1} for **2** and -588×10^{-6} cm^3 mol^{-1} for **3**. All measurements were made at a fixed field strength and the field dependence of the magnetic susceptibility was not studied. The data were fitted by the appropriate theoretical expression for two interacting high-spin iron(III) ions using the usual isotropic spin Hamiltonian $H_0 = -2JS_1S_2$.[19b] Inclusion of terms for the temperature-independent paramagnetic susceptibility (t.i.p.) and for possible sample contamination by a paramagnetic iron(III) impurity exhibiting Curie behaviour yielded the relationship (1) where $x = J/kT$, N, g and k have their usual meanings and χ_{para} is the mole fraction of the iron(III) contaminant.

$$\chi_{calc} = \frac{Ng^2\beta^2}{kT}\left(\frac{2e^{2x} + 10e^{6x} + 28e^{12x} + 60e^{20x} + 110e^{30x}}{1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{20x} + 11e^{30x}}\right) + \frac{Ng^2\beta^2S(S+1)}{3kT}\chi_{para} + \text{t.i.p.} \quad (1)$$

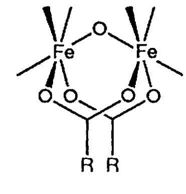
A multiplicative factor $(1 - \chi_{para})$ for the first term was omitted owing to the very small value of χ_{para} in these experiments. A non-linear least-squares fitting computer program was used to fit the observed data. In these calculations g was fixed at 2.00. With all data, J, χ_{para} and t.i.p. were allowed to vary to obtain a best fit as determined by the best R index. The function minimized was $R = (\chi_{exptl} - \chi_{calc})^2/(\chi_{exptl})^2$.

Results and Discussion

Synthetic Aspects.—Since 1983 there has been a growing interest in the syntheses of triply bridged (μ-oxo)bis(μ-carboxylato)-diiron(III) complexes using a variety of tridentate nitrogen-containing capping ligands to model the oxo-bridged dinuclear iron protein haemerythrin. The synthetic strategy adopted has mainly been the 'self-assembly' method of Holm and Ibers.[20] However, our approach resembles that of Lippard and coworkers[4a,6] using preformed $[Fe_2OCl_6]^{2-}$ ion.

Treatment of $[NEt_4]_2[Fe_2OCl_6]$ with sodium acetate or sodium benzoate and the triamine ligands L^1 and L^2 in MeCN at room temperature gave orangish brown solutions which, after work-up and addition of sodium perchlorate, afforded $[Fe_2(\mu\text{-}O)(\mu\text{-}PhCO_2)_2L^1{}_2][ClO_4]_2\cdot 2H_2O$ **1** and $[Fe_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2L^2{}_2][ClO_4]_2\cdot 2H_2O$ **2** as orange-brown microcrystals in *ca.* 50% yield. The synthesis of $[Fe_2(\mu\text{-}O)\{\mu\text{-}(PhO)_2PO_2\}_2L^2{}_2]^{2+}$ was achieved by two different routes, one being similar to that used for the syntheses of **1** and **2** to afford in this case $[Fe_2(\mu\text{-}O)\{\mu\text{-}(PhO)_2PO_2\}_2L^2{}_2][ClO_4]_2\cdot H_2O$ **3** in 50% yield and the other involving an acetate bridge-exchange reaction (see below).

Characterization of the Triply Bridged Core.—The orange-brown solids **1** and **2** showed IR bands typical of bridging acetate and benzoate groups, asymmetric ν(FeOFe) vibration modes,[2b,c] water of crystallization, and ClO_4^-. The presence of NH in the co-ordinated ligand is clearly seen in the IR spectrum of **1**. For **3** the IR bands characteristic of bridging phosphate groups[21] could not be assigned with certainty due to overlapping by the ClO_4^- vibration in the same region. Solution electrical conductivity measurements in acetonitrile solutions reveal that all three compounds are 1 : 2 electrolytes.[22] Magnetic susceptibility measurements at 300 K in such solutions using Evans NMR method[18] gave effective magnetic moments of *ca.* 1.70 per Fe (carboxylate bridge) and 1.86 per Fe (phosphate bridge), typical[2b,c] for triply bridged cores (only carboxylate bridge is shown), and confirm the integrity of these cores in solution.



This core formulation for **1** and **2** seems reasonable, given the similarities in the absorption spectra of these complexes in acetonitrile solution when compared to those of all the structurally characterized dimers of the (μ-oxo)bis(μ-carboxylato)diiron(III) family[2b–d] and of metazidohaemerythrin itself.[2b,23] Many features characteristic of such a core are also present in the phosphate-bridged complex **3**, since the absorption energies and intensities compare well for the two classes of compounds.[21,24,25] The shifts in the d–d transitions on going from **2** to **3** imply that diphenyl phosphates are weaker field ligands than are carboxylates. Interestingly, the $^6A_1 \longrightarrow {}^4T_2$ (^4G) d–d transition for **1** occurs at 733 nm while that of a closely related complex $[Fe_2(\mu\text{-}O)(\mu\text{-}PhCO_2)_2(bpa)_2][ClO_4]_2\cdot H_2O$ is at 704 nm [bpa = bis(2-pyridylmethyl)amine].[25a] This observation underscores the weaker ligand field strength of L^1 compared to bpa and is understandable given the fact that expansion of one chelate ring from five- to six-membered results in a decrease in its ligand field strength.[26]

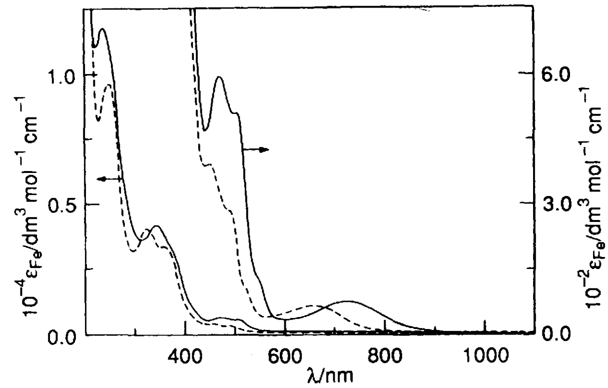


Fig. 1 Carboxylate-exchange reaction of complex **2** with diphenyl phosphate as monitored by absorption spectroscopy in acetonitrile solution: ——, **2**; – – –, after addition of 2 equivalents of $(PhO)_2PO_2H$

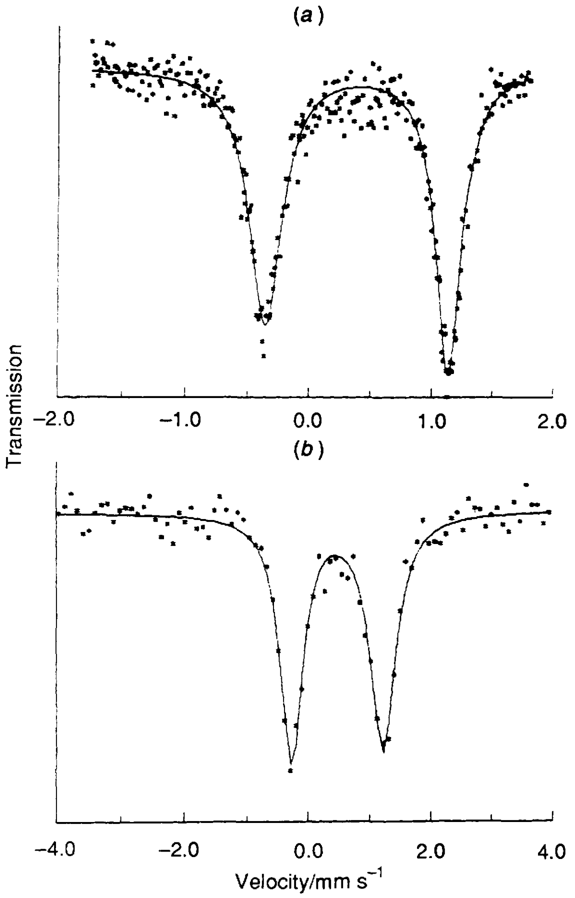


Fig. 2 Zero-field ^{57}Fe Mössbauer spectra of (*a*) complex **3** at 300 K and (*b*) **2** at 77 K, referenced to pure iron metal at 300 K

Carboxylate Bridge-exchange Reactions.—To investigate the lability of the carboxylate bridges in complexes **1** and **2** we have done the following experiments on **2**, *viz*. (*i*) acetate bridge-exchange reaction using deuterioacetic acid and (*ii*) exchange of the acetate bridge by a phosphate bridge.

In complex **2** the bridging acetate groups exchange readily in CD_3CN solution upon addition of 10 equivalents of CD_3CO_2D [equation (2)] as revealed by ^{1}H NMR spectroscopy. The

$$[Fe_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2L^2_2]^{2+} + \text{excess of } CD_3CO_2D \xrightarrow{CD_3CN} [Fe_2(\mu\text{-}O)(\mu\text{-}CD_3CO_2)_2L^2_2]^{2+} \quad (2)$$

spectrum recorded within 10 min of mixing reveals that the bridged diiron(III) structure remains intact and that resonances associated with the CH_3 of the co-ordinated acetate groups (δ 10.5) vanish as the deuterioacetate analogue is formed. Moreover, the entire spectra of **2** and its deuterio analogue are seen in the range δ −10 to +30. This is understandable given the strong antiferromagnetic exchange coupling between the diiron(III) sites (see below).

The phosphate-bridged complex $[Fe_2(\mu\text{-}O)\{\mu\text{-}(PhO)_2PO_2\}_2L^2_2]^{2+}$ could readily be generated at 298 K [equation (3)]. The

$$[Fe_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2L^2_2]^{2+} + 2(PhO)_2PO_2H \xrightarrow{MeCN} [Fe_2(\mu\text{-}O)\{\mu\text{-}(PhO)_2PO_2\}_2L^2_2]^{2+} + 2MeCO_2H \quad (3)$$

UV/VIS spectrum of the resulting solution was recorded (Fig. 1) within 5 min of mixing. The spectrum of the phosphate-bridged dimer generated is identical to that obtained for the isolated species. Thus the acetate bridge-exchange reaction for phosphate proceeds instantaneously. Similar reactions were investigated by Lippard and co-workers.[24]

^{57}Fe *Mössbauer Spectra*.—Iron-57 Mössbauer spectroscopy was utilized to provide a direct probe of the electronic and chemical environment of the dinuclear iron(III) sites in these complexes. Representative zero-field Mössbauer spectra of **2** and **3** at 77 and 300 K respectively are shown in Fig. 2 and the results are in Table 1. Each spectrum consists of a single quadrupole-split doublet, the two lines being of unequal intensity for the room-temperature spectrum. The cause of the asymmetric line broadening is attributed to slow spin–lattice relaxation.[27] This is justifiable given the fact that as the absorber temperature is lowered the components of the quadrupole pair become more equal in intensity. The spectrum at 77 K appears almost symmetric (Fig. 2). The values of the isomer shift (δ) and quadrupole splitting (ΔE_Q) relative to metallic iron at room temperature were obtained from least-squares computer fitting (solid line) of the experimental points assuming Lorentzian line shapes. The parameters obtained from these complexes are characteristic of μ-oxo-bridged dinuclear high-spin iron(III) complexes and proteins in general.[2c,d] For the present complexes the isomer shift values at 300 K lie at the lower end[28] of the range usually observed.[2c] The difference in isomer shift values at 77 and at 300 K may be accounted for by the second-order Doppler shifts (s.o.d.s) arising from the different source and absorber temperatures.

Magnetism.—We have so far been unsuccessful in determining the three-dimensional crystal structure of these compounds because the single crystals grown from many solvents readily lose solvent of crystallization at room temperature. Therefore, we have undertaken detailed variable-temperature (8–300 K) magnetic susceptibility analyses on all three complexes to elucidate the magneto-structural correlation.[29] Measurements were carried out on solid samples.

The temperature dependence of the magnetic susceptibilities of a representative complex is shown in Fig. 3. The plot is as expected for strongly coupled $S = \frac{5}{2}$ dimers.[30] The rapid increase in χ_M at low temperatures is due to the presence of traces of a monomeric high-spin impurity. This is a common feature of μ-oxo-iron(III) complexes. The best-fit J values for these complexes are in Table 1. Given the presence of high-spin Fe^{III}, we constrained g to the free-electron value. It is interesting that the J values are somewhat more negative than found for related complexes (Table 1), implying a better spin exchange in the present systems. In the absence of solid-state structural data it would not be appropriate to attempt a definitive explanation. However the following statement is in order. The presence of unsymmetrical chelate rings in L^1 and L^2 might have increased the asymmetry[25,28b,c] in these compounds which has contributed to a stronger magnetic coupling pathway. By unsym-

Table 1 Magnetic and Mossbauer properties of some selected μ-oxo-diiron(III) complexes

			Mössbauer		
Complex	$-J$/cm^{-1}	μ_{eff} per Fe[a]	T/K	δ/mm s^{-1}	ΔE_Q/mm s^{-1}
$[Fe_2(\mu\text{-}O)(\mu\text{-}PhCO_2)_2L^1{}_2][ClO_4]_2\cdot 2H_2O$	127[b]	1.58	300	0.38	1.68
		(1.68)[c]	77	0.52	1.59
$[Fe_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2L^2{}_2][ClO_4]_2\cdot 2H_2O$	125[b]	1.64	300	0.37	1.29
		(1.70)[c]	77	0.50	1.48
$[Fe_2(\mu\text{-}O)\{\mu\text{-}(PhO)_2PO_2\}_2L^2{}_2][ClO_4]_2\cdot H_2O$	108[b]	1.82	300	0.39	1.49
		(1.86)[c]			
$[Fe_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2L^3{}_2][ClO_4]_2$[d]	115	—	4.2	0.47	1.50
$[Fe_2(\mu\text{-}O)(\mu\text{-}PhCO_2)_2L^4{}_2][ClO_4]_2$[e]	117	1.64	—	—	—
$[Fe_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2L^5{}_2][ClO_4]_2$[f]	120	1.66	100	0.51	1.64
$[Fe_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2\{HB(pz)_3\}_2]$[g]	121	1.71	4.2	0.52	1.60
$[Fe_2(\mu\text{-}O)(\mu\text{-}Me_3CCO_2)_2L^4{}_2][ClO_4]_2$[h]	116	—	293	0.44	1.37
			70	0.55	1.30
$[Fe_2(\mu\text{-}O)\{\mu\text{-}(PhO)_2PO_2\}_2\{HB(pz)_3\}_2]$[i]	97.5	1.82	4.2	0.53	1.60

[a] Solid-state values at 300 K. [b] χ_{para} = 3.947 × 10^{-3} (for **1**), 7.598 × 10^{-3} (for **2**) and 6.397 × 10^{-3} (for **3**). t.i.p. = 2.909 × 10^{-6} (for **1**), −1.819 × 10^{-4} (for **2**) and 5.415 × 10^{-5} (for **3**). [c] Measured in acetonitrile solution by Evans method[18] at 300 K. [d] L^3 = 1,4,7-trimethyl-1,4-7-triazyclononane; ref. 5. [e] L^4 = bis(benzimidazol-2-ylmethyl)amine; ref. 9*a*. [f] L^5 = tris(*N*-methylimidazol-2-yl)phosphine; ref. 10. [g] pz = Pyrazolyl; ref. 4(*b*). [h] Ref. 9(*c*). [i] Ref. 24.

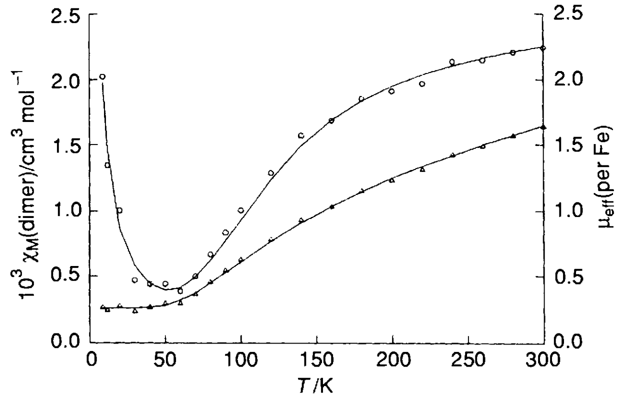


Fig. 3 Molar susceptibility (○) and effective magnetic moment per iron (△) of complex **2** as a function of temperature. The solid lines are theoretical curves calculated as indicated in the text

metrical we mean that no symmetry or pseudo-symmetry operation, other than the identity operation C_1, relates the co-ordination environment around one iron to that around a second.

Conclusion

Our goal of synthesizing diiron(III) complexes containing the triply bridged $[Fe_2(\mu\text{-}O)(\mu\text{-}X)_2]^{2+}$ core [X = $MeCO_2$, $PhCO_2$ or $(PhO)_2PO_2$] has been achieved by using L^1 and L^2 as terminal capping ligands. We have nicely demonstrated that the acetate bridge present in **2** is quite labile. Mössbauer spectral parameters and the temperature dependence of the magnetic susceptibilities point to the presence of two antiferromagnetically coupled diiron(III) centres in these complexes. The extent of exchange coupling observed here is somewhat larger compared to that in many related complexes. We believe that the unsymmetric ligand chelate rings in L^1 and L^2 have caused unfavourable interligand steric interactions and hence introduced asymmetry in the core structure. Using L^2 we have already developed a rich dimanganese chemistry of relevance to biology which will be published elsewhere.

Acknowledgements

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