Iron–Sulphur Dimers with Benzimidazolate–Thiolate, Benzimidazolate–Phenolate, or Bis(benzimidazolate) Terminal Chelating Ligands

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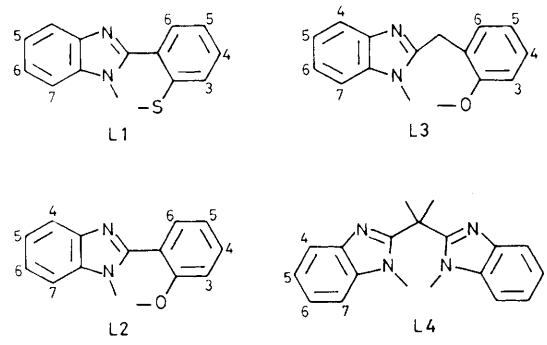
$[Fe_2S_2L_2]^{2-}$ complexes co-ordinated by the mixed-donor N–S, N–O, or N–N ligands L1—L4 are characterised by electronic and n.m.r. spectroscopy and shown to undergo one-electron reduction to the corresponding trianions with e.s.r. spectra exhibiting a range of *g*-tensor values which are compared with those for $[2Fe–2S]^+$ proteins of the Rieske type.

For the Rieske iron–sulphur protein from *Thermus thermophilus* direct evidence has been presented for partial co-ordination of its [2Fe–2S] clusters by two or more non-cysteine ligands.[1] Recent electron nuclear double resonance and electron spin echo data for this protein and for the similar phthalate dioxygenase from *Pseudomonas cepacia* demonstrate that in the reduced form one or more of the ligands is nitrogen, probably from the imidazole ring of a histidine amino acid residue.[2] The rhombic e.s.r. spectra for these two proteins have averaged *g*-values ($g_{av.}$) of *ca.* 1.90[2] which are much lower than the value of *ca.* 1.96 usually associated with thiolate-co-ordinated $[2Fe–2S]^+$ [3,4] Bertrand *et al.*[5] have shown that for these and other [2Fe–2S] proteins having e.s.r. spectra with $g_{av.}$ *ca.* 1.90—1.92 there is a strong correlation between the lowest two *g*-values (g_2 and g_3) and their splitting ($g_2 - g_3$), which may be understood in terms of a variable weak distortion of the co-ordination at the Fe^{2+} ion, comparable to the case for $[Fe_2S_2(SR)_4]^{3-}$ ferredoxins[3] and model complexes.[4] The ligand field model which satisfactorily accounts for the *g*-value correlation in this class of $[2Fe–2S]^+$ centres employs a set of Fe^{2+} energy levels which may be interpreted as arising from a large inequivalence between the bridging sulphur and the terminal ligands. The *g*-tensor for reduced $[Fe_2S_2(OAr)_4]^{2-}$ complexes is a good fit to the $g_{av.}$ *ca.* 1.90—1.92 $[2Fe–2S]^+$ class.[6] It is now of considerable interest to ascertain in detail what range of different co-ordination environments at the Fe^{3+} and more particularly at the Fe^{2+} ion will give rise to a *g*-tensor for the $[2Fe–2S]^+$ centre in keeping with the $g_{av.}$ *ca.* 1.90—1.92 class of proteins. In this communication we report e.s.r. spectra for four $[Fe_2S_2L_2]^{3-}$ complexes co-ordinated by the ligands L1—L4 involving N–S, N–O, and N–N bidentate donors.

NEt_4 and $AsPh_4$ salts of the $[Fe_2S_2L_2]^{2-}$ complexes [(**1**)—(**4**) for L = L1—L4†] were synthesised by ligand exchange with $[Fe_2S_2Cl_4]^{2-}$ as previously described[6,8] (all manipulations were carried out under anaerobic conditions). In initial attempts to prepare a bis(benzimidazolate)-co-ordinated $[2Fe–2S]^{2+}$ complex we employed the ligand 2,2′-methylenebis(benzimidazole) and were surprised to observe in the reaction mixture a strong e.s.r. signal (*g* 2.013, 1.930, 1.875) typical of a $[2Fe–2S]^+$ reduced centre. Only impure pyrophoric paramagnetic solids could be isolated from such reactions. The ligand L4, in which the methylene protons have been replaced by methyl groups, does not cause reduction of the $[2Fe–2S]^{2+}$ centre and thus allows the isolation of a pure reaction product. The $[Fe_2S_2L_2]^{2-}$ complexes are soluble to varying degrees in dimethylformamide (dmf), *N*-methylpyrrolidinone (*N*mp), or dimethyl sulphoxide (dmso) and are stable in solution for prolonged periods. On addition of a small excess of benzene thiol (**2**)—(**4**) convert cleanly into $[Fe_2S_2(SPh)_4]^{2-}$ as monitored by optical spectrophotometry and ^1H n.m.r. spectroscopy.

Electronic absorption spectra of the $[Fe_2S_2L_2]^{2-}$ complexes in dmf are characterised by the following features, λ/nm ($10^{-3}\varepsilon$/dm^3 mol^{-1} cm^{-1}): (**1**) *ca.* 580 sh (7.1), 516 (7.7), *ca.* 435

† L1—L3 were prepared by the method of Sluka *et al.*[7] and L4 by reaction of dimethylpropanedinitrile with *o*-phenylenediamine dihydrochloride at *ca.* 200 °C.



sh (7.5), 300 (52); (**2**) 515 (8.9), 395 (8.7), 331 (37), 292 (41); (**3**) 508 (6.7), 403 (11.0), *ca.* 315 sh, 278 (40); (**4**) 524 (8.3), 408 (8.1), *ca.* 375 sh, 279 (49).

^{1}H N.m.r. spectra at 90 MHz of the complexes in $(CD_3)_2SO$ show the following isotropically-shifted and dipolar-broadened resonances from ligand protons (the assignments in parentheses following the chemical shifts indicate the ring position relative to the donor atom N, S, or O, as marked on the formulae), δ: (**1**) *ca.* −11.15 sh, −10.92 (N-4 and S-6 or S-4), −9.80 (S-4 or S-6), −7.24 and −6.92 (N-6), −5.37 (N-5), −4.45 (S-3), −3.13 (S-5); (**2**) *ca.* −11.4 sh (N-4), −11.31 and −11.02 (O-6 or O-4), −10.84 and −10.66 (O-4 or O-6), −6.98 (N-6), −5.34 (N-5), −3.31 and −2.92 (O-5); (**3**) *ca.* −10.8 sh, −10.50 (N-4, O-4, and O-6), −6.92 (N-6), −5.44 (N-5), −1.98 (O-5), *ca.* −8 (broad underlying $-CH_2-$ resonance); (**4**) −10.61 (N-4), −7.06 (N-6), −5.47 (N-5), *ca.* −3 (broad underlying $-CH_3$ resonance). In each case the proton at the N-7 position is expected to be in close proximity to the Fe such that it is greatly broadened and thus not observed. The resonance at δ −7.06 in (**4**) is broader than those at δ −10.61 or −5.47 and is therefore attributable to the N-6 position. In (**2**) the assignment of the N-5 proton has been established by comparing the spectrum of the corresponding 5,6-methyl-substituted compound for which the peaks at δ −5.34 and −6.98 are absent. Assignments for the other compounds follow from these. The splittings in the chemical shifts of the phenolate protons of (**2**) and the N-6 proton of (**1**), to give two peaks of approximately equal intensity, are presumed to arise from geometric or possibly conformational isomerism.

D.c. polarography of the complexes in dmf shows two reduction waves at a rapid dropping-mercury-electrode (r.d.m.e., *ca.* 6 drops/s): (**1**), $E_{\frac{1}{2}}$ −0.99 (referred to saturated calomel electrode) and −1.86 V; (**2**), −1.09 and −1.96 V; (**3**), −1.13 and −1.95 V; (**4**), −0.82 and −1.81 V. The potentials for the first reduction, assigned to $[2Fe\text{–}2S]^{2+/1+}$, may be compared with those for related $[Fe_2S_2L_4]^{2-}$ complexes measured under the same conditions: L = SPh, $E_{\frac{1}{2}}$ −1.14 V; L = SEt, −1.44 V; 2L = S$_2$-*o*-xylyl, −1.51 V; L = OAr, −1.35 V (average). The mid-point redox potential for the Rieske-type [2Fe–2S] protein from *T. thermophilus* is *ca.* +0.15 V[2] (relative to standard hydrogen electrode) whilst that for benzene dioxygenase from *P. putida* is *ca.* −0.11 V,[9] compared to *ca.* −0.4 V for [2Fe–2S] ferredoxins having four cysteine ligands. Amongst the ferredoxin model complexes cited above $[Fe_2S_2(SEt)_4]^{2-}$ represents the best approximation to co-ordination by four cysteines and leads to positive shifts in $E_{\frac{1}{2}}$ of 620 mV for (**4**) and 350 mV for (**2**) compared to +550 and +290 mV respectively for the *T. thermophilus* and benzene dioxygenase proteins relative to ferredoxins. Although these relative shifts circumvent the difficulties of direct comparisons between models and proteins they may be inadequate to the extent that the Rieske-type [2Fe–2S] proteins most likely have the asymmetric co-ordination

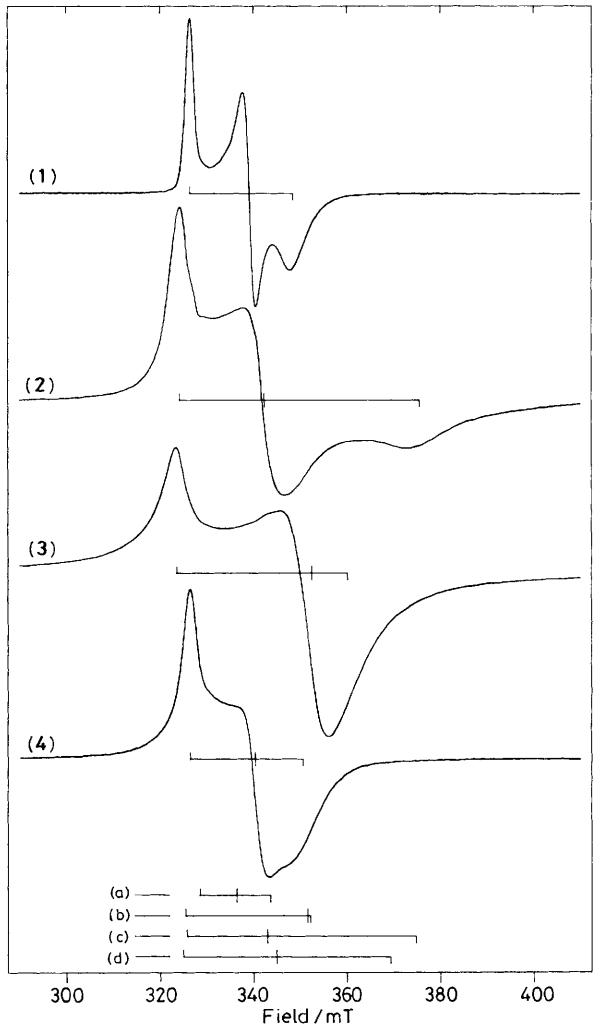


Figure 1. E.s.r. spectra at 77 K and 9.20 GHz of (**1**)—(**4**) reduced in dmf. The marker-lines at the baseline level of each spectrum show the *g*-values derived from simulations, whilst those below show for comparison the *g*-values of (a) $[Fe_2S_2(SPh)_4]^{3-}$ (2.001, 1.954, 1.913),[4] (b) $[Fe_2S_2(OPh)_4]^{3-}$ (2.020, 1.870, 1.867),[6] (c) benzene dioxygenase (2.018, 1.917, 1.754),[9] and (d) the Rieske centre from *T. thermophilus* (2.023, 1.906, 1.78).[2]

$(RS)_2FeS_2FeXY$ (X and Y = imidazolate, imidazole, phenolate, or carboxylate). Cyclic voltammetry of (**1**)—(**4**) at glassy-carbon or platinum electrodes gives well-formed pairs of cathodic current maxima and anodic current minima for the first reduction process, centred at potentials very close to those observed at the r.d.m.e. For (**1**) and (**4**) the cathodic and anodic peak currents are approximately equal.

Reduction of the complexes with sodium acenaphthylenide in dmf[4] gives the trianions with frozen solution e.s.r. spectra as depicted in Figure 1, and the following *g*-values (derived from simulations): (**1**), 2.014, 1.938, 1.886 ($g_{av.}$ 1.946); (**2**), 2.027, 1.920, 1.750 ($g_{av.}$ 1.899); (**3**), 2.031, 1.865, 1.825 ($g_{av.}$ 1.907); (**4**), 2.013, 1.931, 1.875 ($g_{av.}$ 1.940). Similar spectra are observed in *N*mp. In contrast to the instability of all other $[2Fe\text{–}2S]^+$ synthetic complexes so far reported,[4,6,8] reduced (**4**) is stable in solution at ambient temperatures for prolonged periods in the strict absence of molecular oxygen. In $(CD_3)_2SO$ the ^{1}H n.m.r. spectrum of reduced (**4**) shows peaks at δ −12.16 (slightly split), −6.36, and −5.32 which are

slightly narrower than those for the dianion and not greatly different in chemical shift. Thus, no localisation of Fe^{2+} and Fe^{3+} is apparent on the 90 MHz n.m.r. timescale. The reduction of (**4**) proceeds in close to quantitative yield as judged by integration of two peaks in the n.m.r. spectrum relative to the NEt_4 cation or by double integration of the e.s.r. spectrum relative to a Cu-ethylenediaminetetra-acetate standard. Reduction of (**1**) is also quantitative but the resulting trianion is not completely stable. Reduced (**2**) and more particularly reduced (**3**) are somewhat less stable with half lives of *ca.* 1 h and *ca.* 20 min respectively in dmf at room temperature. Interpretation of the *g*-tensors for the complexes and their comparison with those for $[2Fe–2S]^+$ proteins is best achieved by relating them to the splitting of their lowest two values according to the method of Bertrand *et al.*[3,5] A reasonable approximation to distinctions between the types of $[2Fe–2S]^+$ co-ordination is provided by $g_{av.}$ which is *ca.* 1.96 for $[Fe_2S_2(SR)_4]^{3-}$ and *ca.* 1.90—1.92 for the Rieske-type proteins or $[Fe_2S_2(OAr)_4]^{3-}$. Reduced (**1**) and (**4**) are found to be intermediate between these two groupings, whilst reduced (**2**) fits very well into the second group, having *g*-values closely similar to those of benzene dioxygenase (2.018, 1.917, 1.754, $g_{av.}$ 1.896).[9] Reduced (**3**) also lies close to the second group but has rather low values of g_2 and g_3. However, in this case the hyper-Lorentzian lineshape makes it difficult to determine g_3 accurately. These results indicate that imidazolate co-ordination is not as effective as phenolate or carboxylate[8] in lowering g_2 and g_3 from their values in $[Fe_2S_2(SR)_4]^{3-}$ and alone is insufficient to account for their very low values in the Rieske-type proteins having $g_{av.}$ *ca.* 1.91. However, before this conclusion can be extended to distinguish between $(RS)_2Fe^{3+}S_2Fe^{2+}NN$ and $(RS)_2Fe^{3+}S_2Fe^{2+}NO$ as the co-ordination applicable to the Rieske-type proteins it is necessary to know the effects on the *g*-tensor of changes in co-ordination at the Fe^{3+} ion (we have assumed these to be small) and of possible nitrogen co-ordination from imidazole rather than imidazolate.

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