Self assembly of a novel water soluble iron(II) macrocyclic phosphine complex from tetrakis(hydroxymethyl)phosphonium sulfate and iron(II) ammonium sulfate: single crystal X-ray structure of the complex $[Fe(H_2O)_2\{RP(CH_2N(CH_2PR_2)CH_2)_2PR\}]SO_4{\cdot}4H_2O$ (R = CH_2OH)

John C. Jeffery,*[a] Barbara Odell,*[b] Nicola Stevens*[c] and Robert E. Talbot*[c]

[a] *School of Chemistry, University of Bristol, Cantocks Close, Bristol, UK BS8 1TS. E-mail: john.jeffery@bristol.ac.uk*
[b] *Dyson Perrins Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QY.*
E-mail: barbara.odell@chemistry.oxford.ac.uk
[c] *Albright and Wilson UK Ltd., PO Box 80, Trinity Street, Oldbury, West Midlands, UK B69 4LN.*
E-mail: bob_e_talbot@albriw.com

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The water soluble Fe(II) macrocyclic phosphine complex $[Fe(H_2O)_2\{RP(CH_2N(CH_2PR_2)CH_2)_2PR\}]SO_4{\cdot}4H_2O$ (R = CH_2OH) has been characterised by single crystal X-ray diffraction and is formed by a remarkable self-assembly reaction between iron(II) ammonium sulfate and tetrakis(hydroxymethyl)phosphonium sulfate (THPS).

There is increasing interest in catalytic transformations carried out in aqueous media employing water soluble phosphine metal complexes.[1–4] In the latter context, phosphine ligands such as $P(CH_2OH)_3$ have been shown to be useful precursors for the synthesis of water soluble transition metal complexes.[4] Albright and Wilson have an interest in the related phosphonium salt $[P(CH_2OH)_4]_2SO_4$[5] because of its effectiveness as a biocide in oil wells. Recently, it was noted that $[P(CH_2OH)_4]_2SO_4$ also aids the dissolution of iron sulfide deposits and particulates. Iron sulfide arises both from anaerobic microbial activity in oil wells and as a result of indigenous H_2S; deposits cause flow restrictions in vessels and pipework and particulates can upset oil/water separation and lead to damage. In oil well situations, the dissolution of FeS by $[P(CH_2OH)_4]_2SO_4$ is accompanied by a red coloration of produced water from the well. The aim of this study was to explain how $[P(CH_2OH)_4]_2SO_4$ aids the dissolution of FeS and to identify the origin of the resulting red coloration which it was believed might be due to a water soluble iron complex.

The reactions of $[P(CH_2OH)_4]_2SO_4$ and the related phosphine $P(CH_2OH)_3$ with various Fe(II) and Fe(III) salts, *e.g.* FeS, $[Fe(NH_4)_2(SO_4)_2]$, $FeCl_3$, $FeCl_2$ and $FeSO_4$, were investigated to find an iron containing laboratory reagent that would model the red complex formed in the oil wells. Only $[Fe(NH_4)_2(SO_4)_2]$ produced a red colour with $[P(CH_2OH)_4]_2SO_4$ or $P(CH_2OH)_3$ and it was shown that other alkyl phosphonium salts do not give red complexes. Thus it appears that the formation of red water soluble complexes requires an Fe(II) salt, $[P(CH_2OH)_4]_2SO_4$ or $P(CH_2OH)_3$ and, crucially, the presence of ammonium ions. Following optimisation of the reaction conditions it was found that addition of 2 equiv. of $[P(CH_2OH)_4]_2SO_4$ to iron(II) ammonium sulfate in water at room temperature, followed by the slow addition of base (NaOH), so that the pH was maintained between 4.5 and 5.0, immediately produced a deep red solution which gave deep red crystals of $[Fe(H_2O)_2\{RP(CH_2N(CH_2PR_2)CH_2)_2PR\}]SO_4{\cdot}4H_2O$ (R = CH_2OH) **1** on standing at 5 °C for two weeks.

The X-ray crystal structure† of **1** (Fig. 1) reveals a cationic octahedral Fe(II) complex with a remarkable tetradentate phosphine ligand in which alternating phosphorus and nitrogen atoms are linked by CH_2 spacers to form an eight-membered macrocyclic ring which functions as a *cis* bidentate phosphine donor to iron. The two nitrogen atoms carry pendant CH_2PR_2 groups which occupy *trans* diaxial sites in the metal coordination sphere. Two molecules of H_2O occupy the remaining *cis* coordination sites at iron. The complex is highly symmetric and has crystallographically imposed twofold symmetry leading to chemically equivalent pairs of axial and equatorial phosphorus sites. The $^{31}P\{^1H\}$ and ^1H NMR spectra‡ of the low spin d^6 complex **1** are consistent with the solid state structure being maintained in solution. Thus the $^{31}P\{^1H\}$ NMR spectrum shows two triplets at δ 20.1 [t, ^2J(PP) 53 Hz] and −1.5 [t, ^2J(PP) 53 Hz] as expected for the two pairs of chemically inequivalent phosphine sites in the complex.

The precise mechanism by which complex **1** is formed is uncertain but it seems likely that the reaction involves a Mannich-like condensation of $[P(CH_2OH)_4]_2SO_4$ with two ammonium ions, with the iron(II) ion acting as a template which controls the formation of the macrocycle and its pendant phosphine arms. When the reaction of $[P(CH_2OH)_4]_2SO_4$ and iron(II) ammonium sulfate with more prolonged base addition was monitored by 31P{^{1}H} it was observed that the triplets associated with **1** gradually diminished with concomitant

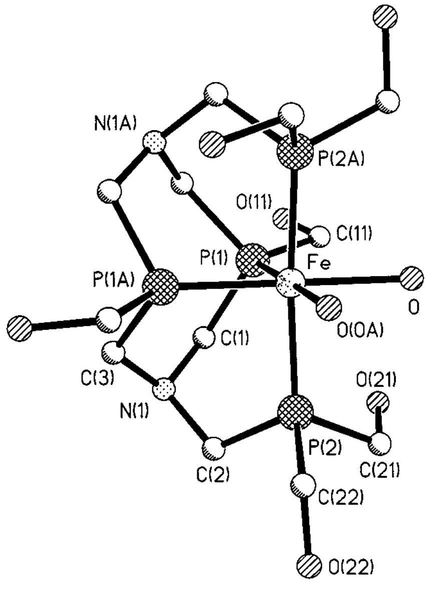
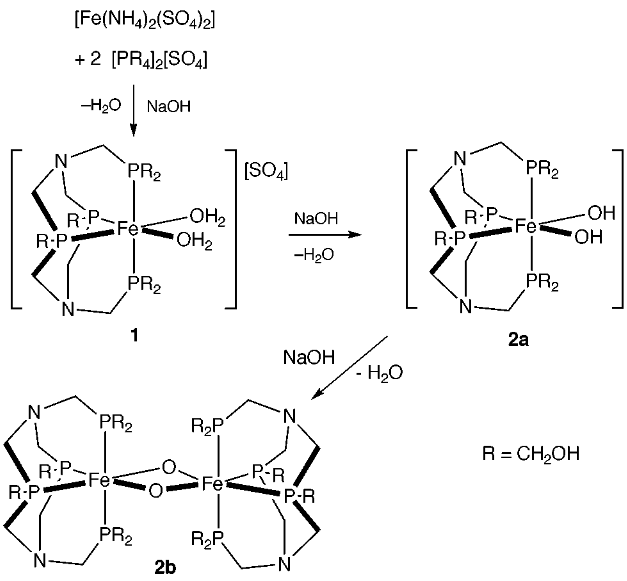


Fig. 1 Molecular structure of the cation of **1** with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Fe–O 2.071(2), Fe–P(1) 2.1797(8), Fe–P(2) 2.2408(8), P(1)–C(11) 1.849(2), P(1)–C(1) 1.865(2), N(1)–C(3) 1.458(2), N(1)–C(1) 1.467(2), N(1)–C(2) 1.475(2), P(2)–C(21) 1.836(2), P(2)–C(22) 1.842(2), P(2)–C(2) 1.845(2); P(1)–Fe–P(1A) 80.63(4), P(1)–Fe–P(2) 92.41(2), O–Fe–P(2) 88.66(5), O–Fe–P(1) 98.25(5), O–Fe–O(OA) 82.87(9), P(2A)–Fe–P(2) 174.89(3), O(OA)–Fe–P(1) 178.87(4), C(3)–N(1)–C(1) 113.7(2), C(3)–N(1)–C(2) 113.0(2), C(1)–N(1)–C(2) 113.0(2).



Scheme 1 Proposed mechanism for formation of **1** and **2**.

formation of a new complex **2** characterised by two new triplet resonances at δ −12.0 [t, ${}^2J$(PP) = 76 Hz] and −22.8 [t, ${}^2J$(PP) 76 Hz]. The latter pattern is very similar to that observed for the complex **1** suggesting a related structure, and although complex **2** has not yet been isolated and fully characterised, we tentatively suggest that it might be a neutral hydroxy **2a** or oxy-bridged complex **2b** of the type shown (Scheme 1) arising from base induced deprotonation of the coordinated H_2O molecules in **1**.

This investigation was stimulated by the need to explain how $[P(CH_2OH)_4]_2SO_4$ aids the dissolution of FeS in oil fields leading to a red coloration of the treated water. The speciation of the Fe/S system in natural environments such as oil wells is necessarily complex but our model reactions allow us to tentatively propose that $[P(CH_2OH)_4]_2SO_4$ and NH_4^+ ions self-assemble iron complexes similar to **1** from FeS that has formed in oil wells owing to sulfate reducing bacteria or indigenous H_2S. The key ammonium ions required for the condensation reaction are usually naturally present in oil field waters where $[P(CH_2OH)_4]_2SO_4$ is used. Also, ammonium bisulfite is often added as an oxygen scavenger to oil field injection water used to pressurise oil-bearing formations, thus providing an additional source. The observation that $[P(CH_2OH)_4]_2SO_4$ and FeS do not appear to react in the absence of NH_4^+ ions, but immediately give red solutions on addition of NH_4^+, adds further support for the proposed mechanism.

Whilst it was not the original intention of this study to prepare new water soluble catalysts, the novel tetradentate macrocyclic phosphine ligand which has been prepared has obvious potential in this context because it imposes facial octahedral coordination whilst leaving two *cis* sites free for potential catalytic transformations. Moreover, the ability of self assembled phosphine ligands of this type to strongly bind transition metals suggests that such systems might have a role to play in waste clean-up procedures. The chemistry involved in the self-assembly of the new Fe complex **1** is novel and a patent has been raised to protect its potential applications.[1]

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Notes and references

† *Crystal data for* **1**: $C_{12}H_{42}Fe\ N_2O_{16}P_4S$, M = 682.3, monoclinic, space group $C2/c$, a = 12.106(4), b = 14.103(6), c = 15.032(4) Å, β = 90.68(2)°, U = 2566(2) Å^3, Z = 4, D_c = 1.766 g cm^{-3}, $F(000)$ = 1432, μ(Mo-Kα) = 0.995 mm^{-1}, $R1$ = 0.030 [$I \geq 2\sigma(I)$], $wR2$ = 0.081 for 2912 unique data, 7820 reflections collected ($2\theta \leq 55°$, 173 K). A full sphere of low temperature data was collected using a Siemens SMART three-circle area detector diffractometer (Mo-Kα X-radiation, graphite monochromator, λ = 0.71069 Å). The structure was solved by direct methods and refined by full matrix least squares on all F^2 data using the SHELXTL 5.03 package on a Silicon Graphics Indy computer.[6] An empirical absorption correction was applied using SADABS.[7] The asymmetric unit contains one half of a molecule of the Fe cation and one half of a disordered SO_4^{2-} anion both lying astride a twofold axis. There are also two molecules of water of crystallisation. CCDC 182/1498. See http://www.rsc.org/cc/a9/a908309j/ for crystallographic files in .cif format.

‡ *Selected spectroscopic data* for **1**: ^{1}H NMR (D_2O, 500 MHz) δ 4.63, 4.56 [AB, 8H, diastereotopic P(CH_2OH)$_2$, ${}^2J$(HH) 13 Hz], 4.37 [s, 4H, P(CH_2OH)], 3.67 (s, 4H, CH_2N), 3.17, 3.10 [AB, 8H, diastereotopic CH_2N, ${}^2J$(HH) 15 Hz]. $^{31}P\{^1H\}$ NMR: δ 20.1 [t, ^{2}P, ${}^2J$(PP) 53 Hz] and −1.5 [t, 2P, ${}^2J$(PP) 53 Hz]. UV–VIS(H_2O) λ_{max} 475 nm, (ε = 1496.0 × 10^{-2} m^2 mol^{-1}). Combined yields of **1** and **2** of *ca.* 88% were estimated by monitoring the conversion of $[P(CH_2OH)_4]_2SO_4$ to products by ^{31}P NMR. Analysis for $C_{12}H_{42}FeN_2O_{16}P_4S$: calc.(obs.) C 21.1 (21.3), H 6.2 (6.5), N 4.1 (4.0%).

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