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Towards Langmuir-Blodgett films of magnetically interesting materials: solution high spin/low spin equilibrium in ambiphilic iron(II) complexes of a triazole-containing ligand

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As a first step towards ambiphilic SCO systems where the hydrophobic part of the system is introduced by a non-coordinating anion (i.e. where no modification of the ligands to introduce hydrophobic substituents is required), [Fe^{II}(OH₂)₂(C₁₆SO₃)₂] and [Co^{II}(OH₂)₂(C₁₆SO₃)₂] have been reacted with the triazole-containing ligands **adpt** and **pldpt** (C₁₆SO₃ = hexadecanesulfonate anion, **adpt** = 4-amino-3,5-bis(2-pyridyl)-1,2,4-triazole, **pldpt** = 4-pyrrolyl-3,5-bis(2-pyridyl)-1,2,4-triazole). In the solid state, HS complexes of the form [Fe^{II}(**Rdpt**)₂(C₁₆SO₃)₂] and [Co^{II}(**Rdpt**)₂(CH₃OH)₂](C₁₆SO₃)₂ are observed, even when excess ligand is used (Rdpt = **adpt** or **pldpt**). In solution, the cobalt complexes remain in this form as evidenced by colour, Visible/NIR and IR spectroscopy. For the iron complexes, there is an equilibrium in solution between the neutral high-spin form of the complex [Fe^{II}(**Rdpt**)₂(C₁₆SO₃)₂] and the dicationic low-spin form [Fe^{II}(**Rdpt**)₃](C₁₆SO₃)₂. Polar solvents favour the dicationic form, while less polar solvents favour the neutral form (as evidenced by solution colour and solution IR spectroscopy). Visible/NIR spectroscopy and Evans' method NMR spectroscopy show the equilibrium can be shifted towards the [Fe^{II}(**Rdpt**)₃](C₁₆SO₃) form by adding additional ligand to the solution. The X-ray crystal structures of [Fe^{II}(**adpt**)₂(C₁₆SO₃)₂] and [Co^{II}(**adpt**)₂(CH₃OH)₂](C₁₆SO₃)₂·1.33CH₃OH are presented. [Fe^{II}(**adpt**)₂(C₁₆SO₃)₂] has a 2D bilayer structure with alternating layers of polar Fe(**adpt**)₂ centres, and hydrophobic alkyl chains. The complex cations in [Co^{II}(**adpt**)₂(CH₃OH)₂](C₁₆SO₃)₂·1.33CH₃OH form 1-D columns in the solid state. The capacity of the amphiphilic complexes [Fe^{II}(**pldpt**)₂(C₁₆SO₃)₂] and [Fe^{II}(**adpt**)₂(C₁₆SO₃)₂] to self-assemble has been probed at the air-water interface using Langmuir techniques. The pertinent pressure-area isotherms reveal only a low tendency of the complexes to form films.

Introduction

The topic of spin crossover (SCO)¹ in first-row transition metal ions, particularly iron(II),² has been the subject of much research. One of the driving forces for this has been the potential applications of SCO in the fields of nanotechnology and molecular electronics.³ To achieve such applications, the metal complexes must be arranged in an orderly fashion. A number of methods have been attempted in this regard: notably, Bousseksou *et al.*⁴ recently assembled [Fe(pyrazine)](Pt(CN)₄) on a gold surface, and observed a hysteretic SCO event, centred around room temperature. One of us recently described a major improvement in the cooperativity of an iron(III) complex through self-assembly in solution.⁵

Other authors have prepared Langmuir-Blodgett (LB) films, or Langmuir monolayers, of iron(II) complexes, and some success in achieving SCO has been realised. These systems have either been polymeric systems of the form {[Fe(4R-trz)₃]X₂}_n, where 4R-trz is a 1,2,4-triazole moiety with a hydrophobic substituent at N⁴ of the triazole ring,⁶ or discrete complexes of the form [FeL₂(NCS)₂], where L represents

either phenanthroline or 2,2'-bipyridine groups that have been modified to contain long alkyl chains.^{7,8}

Recently, Aida *et al.*⁹ reported the preparation of gels of the form [Fe(4R-trz)₃](C_nSO₃)₂, where C_nSO₃ represents the sulfonate derivative of an alkyl chain containing *n* carbon atoms. These systems incorporate hydrophobicity both in the ligand, and in the non-coordinating counterion used (when *n* is large). We are interested to see if this can be extended so that the long-chain alkyl sulfonate counterion is the only part of the system that is hydrophobic. That is, that the central cation, [FeL_n]²⁺, does not require any modification, *i.e.* any neutral ligand(s) could be used, without the need to introduce alkyl chains to the ligand(s). A similar approach was earlier reported by Kurth *et al.*,¹⁰ and more recently by Kimizuka *et al.*¹¹ although these authors used a much more complicated hydrophobic anion, that required significant synthetic effort.

Our interest is in probing whether or not the simple starting material, [Fe^{II}(OH₂)₂(C₁₆SO₃)₂], that Aida *et al.*⁹ reported can be reacted with "normal" ligands (that is, ligands that have not been modified to contain hydrophobic chains) to give iron complexes that self-assemble in solution or at interfaces. This would clearly be hugely advantageous, as a vast number of

systems containing a wide range of ligands could be rapidly synthesized, without first needing to develop synthetic access to hydrophobic-substituent-modified versions of all of the ligands.

As a first step, we have prepared $[\text{Fe}^{\text{II}}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]$ by a slight modification of the method described by Aida *et al.*,⁹ and extended this to prepare the analogous compound, $[\text{Co}^{\text{II}}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]$. We have reacted these two ‘long tailed anion’ reagents with two dipyriddyltriazole-based ligands, 4-amino-3,5-bis(2-pyridyl)-1,2,4-triazole (**adpt**) and 4-pyrrolyl-3,5-bis(2-pyridyl)-1,2,4-triazole (**pldpt**) (Figure 1), as these two ligands are readily prepared and have previously given iron(II) complexes that show SCO behaviour.^{12, 13}

Figure 1. Ligands and counter ion used in this study.

Results and Discussion

Synthesis

The ligands **adpt** and **pldpt** (Figure 1) were prepared in two and three steps, respectively, from commercially available precursors, as previously described (Scheme S1).^{14, 15} We used a modification of Aida *et al.*'s procedure⁹ to prepare the starting material, $[\text{Fe}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]$. These authors report mixing hydrated iron(II) chloride and sodium hexadecanesulfonate in water containing a small amount of ascorbic acid. We have found that sodium hexadecanesulfonate does not dissolve to any great extent at room temperature, and the product, $[\text{Fe}^{\text{II}}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]$ is also insoluble in water. As both materials look very similar, it is difficult to tell when the reaction is complete. We have found that sodium hexadecanesulfonate is reasonably soluble in water at 70 °C, and so we heat sodium hexadecanesulfonate and ascorbic acid to this temperature in water, and add iron(II) chloride tetrahydrate, as a solid, to this hot solution. Stirring at this temperature for ten minutes and then allowing the mixture to cool results in the precipitation of analytically pure $[\text{Fe}^{\text{II}}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]$ in essentially quantitative yield (96%) after washing with cold water, and drying thoroughly *in vacuo* over phosphorus pentoxide. We have found that using one molar equivalent of ascorbic acid for each equivalent of hydrated iron(II) chloride gives the highest purity product. Omitting the ascorbic acid completely gives a pale yellow, rather than white powder, the elemental analysis of which suggests significant oxidation to an iron(III) hydroxo-containing species. The same method was used to prepare $[\text{Co}^{\text{II}}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]$; again, in analytically pure form and essentially quantitative yield (99%).

Initially, three equivalents of ligand were reacted with one equivalent of $[\text{Fe}^{\text{II}}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]$ in methanol, giving dark red solutions. Stirring at room temperature and then either subjecting the reaction mixture to diethyl ether vapour

diffusion, or allowing it to slowly evaporate did not give $[\text{Fe}(\text{Rdpt})_3](\text{C}_{16}\text{SO}_3)_2$ as hoped. Instead, analytically pure $[\text{Fe}(\text{Rdpt})_2(\text{C}_{16}\text{SO}_3)_2]$ was obtained as pale orange microcrystals in reasonable yield (67% for **Rdpt** = **adpt**, 54% for **Rdpt** = **pldpt**). Attempts to carry out the reaction in different solvents were thwarted by the poor solubility of $[\text{Fe}^{\text{II}}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]$ in solvents other than methanol and water, and the poor solubility of the ligands in water.

The reaction of $[\text{Co}^{\text{II}}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]$ with either two or three equivalents of **adpt** or **pldpt** in methanol gave complexes of the form $[\text{Co}^{\text{II}}(\text{Rdpt})_2(\text{CH}_3\text{OH})_2](\text{C}_{16}\text{SO}_3)_2 \cdot \text{solvent}$ in good yield (77%, *solvent* = H_2O for **adpt**, 68%, *solvent* = $0.5\text{CH}_3\text{OH}$ for **pldpt**). As with the analogous iron complexes, complexes of the form $[\text{Co}^{\text{II}}(\text{Rdpt})_3](\text{C}_{16}\text{SO}_3)_2$ could not be accessed, even when using three equivalents of ligand.

The starting materials $[\text{Fe}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]$ and $[\text{Co}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]$ were then reacted with six equivalents of **Rdpt** to see if this larger excess would allow isolation of the $[\text{M}^{\text{II}}(\text{Rdpt})_3](\text{C}_{16}\text{SO}_3)_2$ complexes. The reactions with six equivalents of **pldpt** (the cobalt reaction was refluxed for 30 min to ensure all reagents dissolved; this was not a problem with the iron reaction), after vapour diffusion of diethyl ether into the reaction solution (iron) or slow evaporation of the reaction solution (cobalt), yielded $[\text{Fe}^{\text{II}}(\text{pldpt})_2(\text{C}_{16}\text{SO}_3)_2]$ and $[\text{Co}^{\text{II}}(\text{pldpt})_2(\text{CH}_3\text{OH})_2](\text{C}_{16}\text{SO}_3)_2$ in similar yields and purities to the reactions with three equivalents. In the case of the reactions with six equivalents of **adpt** (again the cobalt reaction was refluxed for 30 min), the resulting complexes were found to be too soluble (on the smaller scales used) to be easily isolated by slow evaporation. Instead, vapour diffusion of diethyl ether into the reaction solutions was used. Only a small amount of $[\text{Fe}^{\text{II}}(\text{adpt})_2(\text{C}_{16}\text{SO}_3)_2]$ was obtained (probably due to its high solubility; the filtrate was still highly coloured), but $[\text{Co}^{\text{II}}(\text{adpt})_2(\text{CH}_3\text{OH})_2](\text{C}_{16}\text{SO}_3)_2$ was obtained in a similar yield and purity to the reaction with three equivalents. In summary, once again it is clear that the nature of the product *isolated* from reactions of these bidentate ligands with first row transition metal ions is not controlled simply by reaction stoichiometry.¹⁴

Spin equilibrium

Both $[\text{Fe}^{\text{II}}(\text{adpt})_2(\text{C}_{16}\text{SO}_3)_2]$ and $[\text{Fe}^{\text{II}}(\text{pldpt})_2(\text{C}_{16}\text{SO}_3)_2]$ exist as pale orange solids in the solid state – typical of high spin (HS) iron(II). However methanol solutions of both are dark red in colour – suggestive of a low spin (LS) iron(II) complex, although the complex of **adpt** is considerably darker than that of **pldpt**. Interestingly, attempts to recrystallise the complexes from non-polar solvents (cyclohexane, toluene) gave pale yellow solutions/suspensions, while using more polar solvents [tetrahydrofuran (THF), methanol] gave red solutions. When $[\text{Fe}^{\text{II}}(\text{adpt})_2(\text{C}_{16}\text{SO}_3)_2]$ was suspended in cyclohexane or toluene, adding a few drops of methanol caused the yellow suspension to turn red, while about 25% by volume THF was required to effect the same colour change.

We have previously prepared the complexes $[\text{Fe}^{\text{II}}(\text{adpt})_3](\text{BF}_4)_2$ and $[\text{Fe}^{\text{II}}(\text{pldpt})_3](\text{BF}_4)_2$, which are LS at room temperature, and are rich red-colours.¹³ Given this, and

the fact that C_{16}SO_3 is typically a non-coordinating anion, we hypothesise that there is an equilibrium in solution between, at least, the dicationic LS tris complex, $[\text{Fe}^{\text{II}}(\text{Rdpt})_3](\text{C}_{16}\text{SO}_3)_2$ and the neutral HS complex $[\text{Fe}^{\text{II}}(\text{Rdpt})_2(\text{C}_{16}\text{SO}_3)_2]$. Non-polar solvents presumably lead to stabilisation of the neutral (HS) species containing non-coordinated anions, while the addition of a more polar solvent stabilises the positively charged (LS) cationic species.

Similar solution equilibria have been a feature of all of our studies with these potentially bis-bidentate **Rdpt** ligands and iron(II), adding considerable complexity.^{13, 16}

UV/Vis/NIR spectroscopy

To investigate this further, methanol and dichloromethane solutions of $[\text{Fe}^{\text{II}}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]$, with various amounts of

Figure 2. UV/Vis/NIR spectra in MeOH for $[\text{Fe}^{\text{II}}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]:\text{adpt}$ in (a) 1:2 ratio (blue), (b) 1:3 ratio (maroon), (c) 1:6 ratio (green).

Rdpt ligand, were investigated between 400 nm and about 1100 nm using UV/Vis/NIR spectroscopy. Two bands are observed in the spectra of all of these solutions: a reasonably sharp and strong band at approximately 480 nm, probably resulting from the LS form of the compound, and a much weaker, and very broad band at 900–1100 nm probably due to d-d transitions of the HS form (Figure 2, Figures S1 & S2).

Due to the probable existence of a mixture of solution species, extinction coefficients cannot be calculated reliably per complex, hence they are provided per $\text{Fe}(\text{II})$, which will be an underestimate of the true values. When one equivalent of metal salt is combined with two equivalents of **adpt** in methanol the band at 480 nm ($\epsilon = 3040 \text{ L mol}^{-1} \text{ cm}^{-1}$) is 70 times more intense than the band at 1119 nm ($\epsilon = 45 \text{ L mol}^{-1} \text{ cm}^{-1}$). Changing this $\text{Fe}(\text{II}):\text{adpt}$ ratio to 1:3 causes the intensity of the 480 nm band to increase and the 1119 nm band to decrease, so that the higher energy band is 1,500 times more intense, while with six equivalents of ligand this band is more intense than that at 1119 nm by a factor of 2,000. When the experiment was repeated using **pldpt** the higher energy band, at 471 nm ($\epsilon = 445 \text{ L mol}^{-1} \text{ cm}^{-1}$), was only 7 times more intense than the lower energy band at 1113 nm ($\epsilon = 64 \text{ L mol}^{-1} \text{ cm}^{-1}$) when two equivalents of ligand were used, rising to 300 times more intense with three equivalents of ligand, and 1,000 times more intense with six equivalents of ligand.

Unfortunately, the solubility of the complexes in non-polar hydrocarbon solvents was not sufficient to collect UV/Vis/NIR data. Spectra were run in CH_2Cl_2 , but the low

solubility only allowed observation of the more intense higher energy band (when investigating this band in methanol, concentrations of 20 mmol L^{-1} were necessary to observe the longer wavelength low intensity signal). The $\sim 480 \text{ nm}$ band decreases in intensity when switching from methanol to CH_2Cl_2 (by a factor of 1.2 for **adpt** and a factor of 3 for **pldpt**).

These results are consistent with the hypothesised equilibrium of LS and HS forms of the complex in solution. Increasing the amount of **Rdpt** present in solution increases the intensity of the LS band at 480 nm, presumably because it drives the equilibrium towards the LS $[\text{Fe}(\text{Rdpt})_3]^{2+}$ species, simultaneously reducing the intensity of the band at $\sim 1100 \text{ nm}$ arising from the HS $[\text{Fe}(\text{Rdpt})_2(\text{C}_{16}\text{SO}_3)_2]$ species.

UV/Vis/NIR spectra of the cobalt(II) complexes showed very little absorption over the range 400–1500 nm. Very weak bands ($\epsilon \sim 40 \text{ L mol}^{-1} \text{ cm}^{-1}$) are observed at $\sim 460 \text{ nm}$.

Solid state and solution IR spectroscopy

The solid state IR spectrum of $[\text{Fe}^{\text{II}}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]$ shows a strong band at 1161 cm^{-1} , which we attribute to the asymmetric S=O stretch of the coordinated sulfonate group. The solid state IR spectra of $[\text{Fe}^{\text{II}}(\text{adpt})_2(\text{C}_{16}\text{SO}_3)_2]$ and $[\text{Fe}^{\text{II}}(\text{pldpt})_2(\text{C}_{16}\text{SO}_3)_2]$ show this band at 1159 and 1149 cm^{-1} respectively (similar to the 1145 cm^{-1} band observed for $[\text{Cu}^{\text{II}}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]$,¹⁷ although different to Aida *et al.*, who report this band at 1196 cm^{-1} in $[\text{Fe}^{\text{II}}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]$ ⁹). The solid state IR spectra of $[\text{Co}^{\text{II}}(\text{adpt})_2(\text{CH}_3\text{OH})_2](\text{C}_{16}\text{SO}_3)_2$ and $[\text{Co}^{\text{II}}(\text{pldpt})_2(\text{CH}_3\text{OH})_2](\text{C}_{16}\text{SO}_3)_2$ show bands at 1170 and 1172 cm^{-1} respectively, which we attribute to asymmetric S=O stretches of the non-coordinated sulfonate group.

Solution state IR spectra of the metal complexes were recorded in CH_2Cl_2 and 9:1 CH_2Cl_2 :methanol – unfortunately the nature of the solution IR cell prohibits the use of any more polar solvents or solvent mixtures, as these would dissolve the KBr window of the cell. Neither $[\text{Fe}^{\text{II}}(\text{adpt})_2(\text{C}_{16}\text{SO}_3)_2]$ or $[\text{Fe}^{\text{II}}(\text{pldpt})_2(\text{C}_{16}\text{SO}_3)_2]$ have high solubility in CH_2Cl_2 or 9:1 CH_2Cl_2 :methanol, so the background noise in the spectra is quite high: nevertheless, we were able to obtain some useful data regarding the nature of the species present in solution.

The solution spectrum of one equivalent of $[\text{Fe}^{\text{II}}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]$ and two equivalents of **pldpt** in CH_2Cl_2 shows the asymmetric S=O stretch at 1150 cm^{-1} – the same frequency as observed in the solid state spectrum of $[\text{Fe}^{\text{II}}(\text{pldpt})_2(\text{C}_{16}\text{SO}_3)_2]$, within the accuracy of our instrument. A very weak band appears to be present at $\sim 1190 \text{ cm}^{-1}$ (see later in this paragraph). Adding an additional equivalent of ligand did not alter the spectrum in the sulfonate stretching region, implying that the neutral $[\text{Fe}^{\text{II}}(\text{pldpt})_2(\text{C}_{16}\text{SO}_3)_2]$ form of the complex is the major form of the complex in the non-polar solvent CH_2Cl_2 . In contrast, the spectrum of one equivalent of $[\text{Fe}^{\text{II}}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]$ and two equivalents of **pldpt** in 9:1 CH_2Cl_2 :methanol shows a significant shift in the asymmetric S=O stretch: the band broadens, and moves to 1192 cm^{-1} . We tentatively attribute this shift to a non-coordinated sulfonate group, arising because the methanol solvent is coordinating in the axial positions. This band is in a similar position to that observed

by Aida *et al.* for non-coordinated hexadecanesulfonate anions in $\{[\text{Fe}(\text{4R-trz})_3](\text{C}_{16}\text{SO}_3)_2\}_\infty$ – these were observed between 1207 and 1213 cm^{-1} , depending on the spin state of the iron(II) complex.⁹ Adding an extra equivalent of ligand does not cause this band to move, suggesting the $[\text{Fe}^{\text{II}}(\text{Rdpt})_3]^{2+}$ species is not involved in any equilibria in this solvent mixture.

Unfortunately, the solubility of $[\text{Fe}^{\text{II}}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]/\text{adpt}$ mixtures in CH_2Cl_2 was too low to allow useful solution IR spectra to be run. The spectra of 1:2 and 1:3 mixtures of $[\text{Fe}^{\text{II}}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]$ and **adpt** in 9:1 CH_2Cl_2 :methanol are very similar to those observed for the analogous **pldpt**-containing mixtures.

To summarise: in straight CH_2Cl_2 , mixtures of $[\text{Fe}^{\text{II}}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]$ and **pldpt** seem to exist predominantly as the neutral form of the complex, *i.e.* $[\text{Fe}^{\text{II}}(\text{pldpt})_2(\text{C}_{16}\text{SO}_3)_2]$. Addition of a small amount of methanol (10% by volume) seems to cause the replacement of the coordinated sulfonate anions with methanol, leading to non-coordinated anions. Solubility of **adpt**-containing complexes in CH_2Cl_2 was too low to allow useful results to be obtained.

Evans' NMR method

The magnetic susceptibility of the complexes in solution was examined using the Evans' NMR method.¹⁸ The methanol-methyl signal of an 11 mmol L^{-1} solution of $[\text{Fe}^{\text{II}}(\text{adpt})_2(\text{C}_{16}\text{SO}_3)_2]$ in d_4 -methanol shifted downfield (0.358 ppm, $\Delta f = 107$ Hz) relative to a capillary of blank solvent, corresponding to a magnetic susceptibility of about 5.1 B.M. per iron(II) centre. This is consistent with the majority of the solution being in the HS $[\text{Fe}^{\text{II}}(\text{adpt})_2(\text{C}_{16}\text{SO}_3)_2]$ form, possibly with a small contribution from a LS $[\text{Fe}^{\text{II}}(\text{adpt})_3]^{2+}$ (any such contribution would be partially masked, as with only two equivalents of **adpt** per iron centre, a maximum of 2/3 of the complex could be present in the LS form). Adding an extra equivalent of ligand caused the d_4 -methanol shift to all but disappear (0.028 ppm, $\Delta f = 8$ Hz), corresponding to a magnetic susceptibility of ~ 0 B.M., suggesting that the vast majority of the complex is present as the LS $[\text{Fe}^{\text{II}}(\text{adpt})_3]^{2+}$ form when the $\text{Fe}(\text{II}):\text{adpt}$ ratio is 1:3. In the case of $[\text{Fe}^{\text{II}}(\text{pldpt})_2(\text{C}_{16}\text{SO}_3)_2]$, the methanol-methyl signal of an 16 mmol L^{-1} solution of $[\text{Fe}^{\text{II}}(\text{pldpt})_2(\text{C}_{16}\text{SO}_3)_2]$ in d_4 -methanol shifted downfield (0.422 ppm, $\Delta f = 140$ Hz) relative to a capillary of blank solvent, corresponding to a magnetic susceptibility of about 5.4 B.M. per iron(II) centre. Adding an extra equivalent of ligand caused the d_4 -methanol signal to shift 0.152 ppm ($\Delta f = 140$ Hz) ppm relative to the blank solvent, corresponding to a magnetic susceptibility of about 3.3 B.M. indicating a transition by some, but not all, of the HS $[\text{Fe}^{\text{II}}(\text{pldpt})_2(\text{C}_{16}\text{SO}_3)_2]$ molecules to the LS $[\text{Fe}^{\text{II}}(\text{pldpt})_3]^{2+}$.

Behaviour of the complexes at the air-water interface

The capacity of the amphiphilic complexes $[\text{Fe}^{\text{II}}(\text{pldpt})_2(\text{C}_{16}\text{SO}_3)_2]$ and $[\text{Fe}^{\text{II}}(\text{adpt})_2(\text{C}_{16}\text{SO}_3)_2]$ to self-assemble has been probed at the air-water interface using

Langmuir techniques.¹⁹ The pertinent pressure-area isotherms reveal only a weak tendency of the complexes to form stable films. Substantial surface pressures were only measured when complex concentrations were high (Figure S3 & S4). Moreover, these films displayed very limited stability and within a few minutes, the surface pressure dropped essentially to the original level. These observations are in agreement with a certain degree of water solubility of the complexes, or parts of the complexes, thus generating micelle type structures in equilibrium with surface-active complexes arranged at the air-water interface.

Most strikingly, the pressure-area isotherms indicate identical molecular surface areas irrespective of whether $[\text{Fe}^{\text{II}}(\text{pldpt})_2(\text{C}_{16}\text{SO}_3)_2]$, $[\text{Fe}^{\text{II}}(\text{adpt})_2(\text{C}_{16}\text{SO}_3)_2]$, or the *aqua* complex $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6(\text{C}_{16}\text{SO}_3)_2]$ were employed for film fabrication (Figure 3). Apparently, the **Rdpt** fragment dissociates from the complex into the water layer, resulting in surface active components that are composed of the solvated iron sulfonate only. Such a model is corroborated by the coordinative lability of the iron complexes in solution noted previously (see above). Further support for such a conclusion comes from the small area that was measured per molecule, *ca.* 10 $\text{\AA}^2$ per $\text{Fe}(\text{sulfonate})_2$ unit. Such an area is far too small for an amphiphile comprising two alkyl chains (*cf.* 22 $\text{\AA}^2/\text{molecule}$ determined for a single alkyl chain in behenic acid²⁰). Such a small number can, however, be accounted for if the actual concentration of molecules at the surface is far lower than the originally spread one.²¹

Figure 3. Representative pressure-area isotherms for Langmuir films prepared from $[\text{Fe}^{\text{II}}(\text{pldpt})_2(\text{C}_{16}\text{SO}_3)_2]$ (green), $[\text{Fe}^{\text{II}}(\text{adpt})_2(\text{C}_{16}\text{SO}_3)_2]$ (red), and $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6(\text{C}_{16}\text{SO}_3)_2]$ (blue), indicating identical molecular areas for all films.

X-ray crystallography

Single crystals of $[\text{Fe}^{\text{II}}(\text{adpt})_2(\text{C}_{16}\text{SO}_3)_2]$ were grown as orange plates by the slow evaporation of the methanol reaction solution. One complete complex is present in the asymmetric unit, with no solvent present (Figure 4). The iron(II) centre coordinates two hexadecanesulfonate anions, which bind in a monodentate fashion in the axial positions.

The equatorial sites are occupied by two **adpt** ligands, each binding in a bidentate manner, through one pyridine nitrogen and one triazole nitrogen atom. Bond lengths range from 2.096(2)-2.198(3) Å, and *cis* donor-Fe-donor angles from 75.52(10)-104.35(10)°, typical of high spin Fe(II). Iron-sulfonate bonds are the shortest [2.096(2), 2.101(2) Å], followed by iron-triazole bonds [2.123(3), 2.134(3) Å], with iron-pyridine bonds longer again [2.197(3), 2.198(3) Å] (see Table S1 for full details of all metal-donor bond lengths and angles). Small twists are observed between the coordinated pyridine and triazole rings [5.07(19), 5.55(19)°] with slightly larger twists seen between the non-coordinated pyridine and triazole ring [8.8(2), 11.5(2)°]. Overall the Fe(**adpt**)₂ core is very close to planar.

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One of the two amino protons on each ligand hydrogen-bonds to the nitrogen atom of the non-coordinated pyridine ring [N-H...N = 2.870(4), 2.875(4) Å; <N-H...N = 129.5, 139.6°] (Figure S5). The other amino proton on each ligand strand forms a reasonably strong hydrogen-bond to a sulfonate oxygen atom from an adjacent complex [N-H...N = 2.885(4), 2.998(4) Å; <N-H...N = 136.6, 136.0°, Figure S5]. Moderate offset parallel π - π stacking (Figure S6) is seen between pyridine rings [centroid...centroid = 3.5944(18) Å, 3.711(2) Å; mean plane intersects = 0.0, 5.6°]. The hydrogen-bonding and π - π stacking combine to arrange the iron-**adpt** centres into 2D-sheets, which alternate with 2D-sheets of alkyl chains (Figures 5 & S7) to give the complex a bilayered structure.

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Figure 4. Perspective view of [Fe^{II}(**adpt**)₂(C₁₆SO₃)₂]. Hydrogen atoms omitted for clarity.

Single crystals of $[\text{Co}^{\text{II}}(\text{adpt})_2(\text{CH}_3\text{OH})_2](\text{C}_{16}\text{SO}_3)_2 \cdot 1.33\text{CH}_3\text{OH}$ were grown as large orange blocks by the slow evaporation of the methanol reaction solution. One and a half complexes and two methanol solvents of crystallisation are present in the asymmetric unit, with the rest of the complex generated by a centre of inversion located on the cobalt ion of the half-complex (Figure 6). Two methanol groups coordinate in the axial sites, with two **adpt** ligands coordinating in a bidentate manner in the equatorial plane. Bond lengths range from 2.0682(13) to 2.1577(15) Å and *cis* donor-Co-donor angles range from 76.73(6) to 104.67(6)°, typical of HS Co^{II} . Very small twists are seen between the coordinated pyridine and triazole rings [1.91(11) to 5.03(11)°], with slightly larger twists between triazole and non-coordinated pyridine rings [7.67(11) to 10.67(11)°]. These small twists keep the $\text{Co}(\text{adpt})_2$ core very close to planar.

Very strong hydrogen bonds are seen between the coordinated methanol groups and sulfonate oxygens [$\text{O}\cdots\text{H}\cdots\text{O} = 2.5831(19)\text{--}2.6144(19)$ Å, $\angle\text{O}\cdots\text{H}\cdots\text{O} = 167.9\text{--}177.5^\circ$] (Figure 6), with weaker hydrogen bonds between the methanol solvates and other sulfonate oxygen atoms [$\text{O}\cdots\text{H}\cdots\text{O} = 2.756(2)\text{--}2.778(2)$ Å, $\angle\text{O}\cdots\text{H}\cdots\text{O} = 156.7\text{--}163.0^\circ$] (Figure S8). One proton from each amino group hydrogen bonds to the non-coordinated pyridine nitrogen atom from the same ligand strand [$\text{N}\cdots\text{H}\cdots\text{N} = 2.861(2)\text{--}2.887(2)$, $\angle\text{N}\cdots\text{H}\cdots\text{N} = 134.3$ to 137.6°], with the other hydrogen-bonding to a sulfonate group [$\text{N}\cdots\text{H}\cdots\text{N} = 2.849(2)\text{--}2.903(2)$, $\angle\text{N}\cdots\text{H}\cdots\text{N} = 160.6$ to 164.3°]. As well as two hydrogen bonds (one to a coordinated methanol, and one to an amino proton), each sulfonate group is involved in an anion- π interaction with the triazole ring [centroid $\cdots\text{O} = 2.8878(17)\text{--}2.9631(17)$ Å], so that each of the three sulfonate oxygen atoms is involved in some form of interaction. These close contacts arrange the complex cations in 1-D columns, with each column having its $\text{Co}(\text{adpt})_2$ planes perpendicular to the adjacent column (Figure S9). No significant π - π stacking is observed. For full details of the supramolecular interactions in both complexes see Tables S2-S4.

Figure 5. View of packing down the *a*-axis of $[\text{Fe}^{\text{II}}(\text{adpt})_2(\text{C}_{16}\text{SO}_3)_2]$. Hydrogen atoms omitted for clarity.

Figure 6. Perspective view of $[\text{Co}^{\text{II}}(\text{adpt})_2(\text{CH}_3\text{OH})_2](\text{C}_{16}\text{SO}_3)_2 \cdot 1.33\text{CH}_3\text{OH}$. Solvent molecules and hydrogen atoms, except the methanol OH protons, omitted for clarity.

Conclusions

Herein we provide details of a refined, high yielding (96-99%) synthesis of pure $[\text{Fe}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]$ and $[\text{Co}(\text{OH}_2)_2(\text{C}_{16}\text{SO}_3)_2]$. Using these two versatile reagents we have prepared two iron(II) and two cobalt(II) complexes of two N^4 -substituted 3,5-bis(2-pyridyl)-1,2,4-triazole (**Rdpt**) ligands. These four complexes contain either coordinated or closely-associated C_{16}SO_3 anions. The X-ray crystal structure determinations carried out on two of these complexes show that these anions facilitate the complex molecules packing via interdigitation of the long hydrophobic alkane portion of the anion.

In the solid state, all four complexes are HS $[\text{M}(\text{Rdpt})_2\text{X}_2]^{n+}$, where M is Fe or Co, X is solvent or anion and n is 2 or 0, respectively. In methanol solution, the cobalt complexes remain in the $[\text{M}(\text{Rdpt})_2\text{X}_2]^{n+}$ form, even in the presence of three equivalents of ligand per metal ion. In contrast, in the case of iron(II), solution studies (UV/Vis/NIR, IR, Evans method NMR) are consistent with the addition of a third equivalent of ligand promoting formation of LS tris complexes, of the form $[\text{Fe}(\text{Rdpt})_3]^{2+}$. When $\text{R} = \text{NH}_2$ (**adpt**), the conversion to the tris form is virtually complete and is accompanied by a drop in the

effective magnetic moment (as determined by Evans method NMR studies). However, when R is a pyrrole ring (**pldpt**), the conversion to the LS form is either not total, or the tris complex is still partially HS,¹³ because the magnetic moment lies between those expected for the HS and LS forms.

Despite the results of these solution studies, especially those for iron(II) and **adpt**, and despite one's intuitive feeling that the isolation of the tris complexes should be straightforward, this is not the case. The solids obtained, regardless of whether a 1:2 or 1:3 metal:ligand ratio was used in the reactions, were pure $[\text{M}(\text{Rdpt})_2\text{X}_2]^{n+}$, not $[\text{M}(\text{Rdpt})_3]^{2+}$, complexes. This contrasts with the results of our studies of $[\text{Fe}(\text{Rdpt})_3]^{2+}$ complexes with PF_6^- counter ions,¹³ but is consistent with our general experience with the **Rdpt** ligands - that the nature of the product is not at all easily controlled, as it is influenced by many factors,^{14,16} and certainly choice of reaction stoichiometry alone is not sufficient.

Pressure-area isotherms of Langmuir films of $[\text{Fe}(\text{Rdpt})_2(\text{C}_{16}\text{SO}_3)_2]$ ($\text{R} = \text{NH}_2$ and pyrrolyl) show that both complexes have only a weak tendency to form films and that these films are unstable. Therefore our attentions are now focussed on the preparation of the long-chain alkyl sulfonate, C_{16}SO_3 , salts of iron complexes that are far more robust in solution than the present *bidentate* ligand complexes have proven to be. The first such target is the C_{16}SO_3 analogue of the SCO active diiron(II) complex of the *bis-terdentate* ligand **PMAT**, $[\text{Fe}^{\text{II}}_2(\text{PMAT})_2](\text{BF}_4)_4$.²² We anticipate that such complexes will remain intact in solution, allowing the *synthetically simple* and *potentially widely applicable* 'long tailed anion' approach to preparing films of SCO active species to be truly tested.

Experimental Section

General remarks

IR spectra were recorded as pressed KBr discs on a Perkin Elmer Spectrum BX FT-IR spectrophotometer between 400 and 4000 cm^{-1} . UV/Vis/NIR spectra were recorded on a Varian CARY 500 Scan UV/Vis/NIR spectrophotometer between 200 and 2000 nm. ESI mass spectra were recorded at the University of Otago on a Bruker MicroTOF_Q spectrometer in acetonitrile.

Solution magnetic moments were measured by the Evan's method in CD_3OD using CH_3OH as the chemical shift reference¹⁸ in a double walled NMR tube on a 300 MHz Varian INOVA-300 spectrometer at 25°C. The concentrations employed and observed shifts of the methyl signal are given in the text.

Single crystal X-ray diffraction data were collected on a Bruker Kappa Apex II area diffractometer (University of Otago) at 83 K. In all cases graphite monochromated Mo-K_α radiation ($\lambda = 0.71073 \text{ \AA}$) was used. Both data sets were corrected for absorption using SCALE.²³ The structures were solved using SHELXS-97.²⁴ Both structures were refined against F^2 using all data by full matrix least squares techniques with SHELXL-97.²⁴ All non-hydrogen atoms were modelled anisotropically. Hydrogen atoms were inserted at calculated positions, except for amino protons, and rode on the atoms to which they are attached (including isotropic thermal parameters which were equal to 1.2 times the attached non-hydrogen atom). The amino protons were found in the map and their coordinates fixed. Crystal structure determination details are summarized in Table 1. Neither structure contained any disorder.

Adpt and **pldpt** were prepared by literature methods;^{14, 15} all other materials were bought commercially and used as received. Solvents were laboratory reagent grade and used without purification.

Pressure-area isotherms and time stability were measured at 25 °C on a KSV MiniMicro Langmuir-Blodgett trough with a surface area range from 1700 to 8700 mm^2 . Water was purified with a Barnstead Nanopure

system, and its resistivity was measured to be higher than 18 MΩ cm. Chloroform (puriss. p.a. ≥ 99.8%, Fluka) was used as spreading solvent for [Fe^{II}(pdppt)₂(C₁₆SO₃)₂] and a 97:3 mixture of chloroform/MeOH for [Fe^{II}(adpt)₂(C₁₆SO₃)₂] and [Fe^{II}(H₂O)₂(C₁₆SO₃)₂]. Drops of the surfactant solution (typically 30 μL, 1.00 mM solution) were deposited using a microsyringe on the water subphase. After letting the solvent evaporate for 30 min, the barriers were compressed at 6 mm min⁻¹ rate (corresponding to 3 cm² min⁻¹) and the surface pressure was monitored using a platinum Wilhelmy plate.

10 [Fe^{II}(OH)₂(C₁₆SO₃)₂]

Distilled water (150 mL), containing ascorbic acid (0.176 g, 1.00 mmol) was heated to 70°C. To this was added sodium hexadecanesulfonate (0.657 g, 2.00 mmol), which dissolved to give a colourless solution. Solid iron(II) chloride tetrahydrate (0.199 g, 1.00 mmol) was added at this temperature resulting in the formation of a small amount of white solid. The mixture was heated at 70°C for a further fifteen minutes and then cooled to 4 °C, resulting in the precipitation of a large amount of white solid. This was isolated by filtration, washed with cold distilled water (20 mL) and dried thoroughly over phosphorus pentoxide *in vacuo*. Yield: 0.676 g (96%). FeC₃₂H₇₀O₈S₂: calc. C 54.68, H 10.04, S 9.12; found C 54.92, H 10.17, S 8.80%. IR (KBr, *inter alia*): ν / cm⁻¹ = 2918, 2847, 1652, 1466, 1230, 1221, 1161, 1066, 800, 721, 604. ESI-MS (pos.): m/z = 702.3857 [Fe(OH)₂(C₁₆SO₃)₂]⁺, 379.1687 [Fe(OH)₂(C₁₆SO₃)]⁺, 361.1677 = [Fe(C₁₆SO₃)]⁺.

25 [Co^{II}(OH)₂(C₁₆SO₃)₂]

Distilled water (150 mL) was heated to 70 °C. To this was added sodium hexadecanesulfonate (0.657 g, 2.00 mmol), which dissolved to give a colourless solution. Solid cobalt(II) chloride hexahydrate (0.238 g, 1.00 mmol) was added at this temperature resulting in the formation of a small amount of pale pink solid. The mixture was heated at 70 °C for a further fifteen minutes and then cooled to 4 °C, resulting in the precipitation of a large amount of pale pink solid. This was isolated by filtration, washed with cold distilled water (20 mL) and dried thoroughly over phosphorus pentoxide *in vacuo*. Yield: 0.693 g (99%). CoC₃₂H₇₀O₈S₂: calc. C 54.44, H 9.99, S 9.08; found C 54.68, H 10.20, S 8.88%. IR (KBr, *inter alia*): ν / cm⁻¹ = 2919, 2847, 1663, 1636, 1467, 1235, 1162, 1062, 800, 722, 603. ESI-MS (pos.): m/z = 728.8589 Na⁺[Co(OH)₂(C₁₆SO₃)₂]⁺, 382.1699 [Co(OH)₂(C₁₆SO₃)]⁺, 364.1699 [Co(C₁₆SO₃)]⁺.

[Fe^{II}(adpt)₂(C₁₆SO₃)₂]

40 [Fe^{II}(OH)₂(C₁₆SO₃)₂] (105 mg, 0.15 mmol) and **adpt** (71 mg, 0.30 mmol) were placed in a sample tube. Methanol (10 mL) was added, which caused the white powders to dissolve to form a clear, red solution. This was stirred at room temperature, open to the air, for 1.5 hours and then left open to the air to slowly evaporate. The resulting pale orange crystals were filtered, washed with ice-cold methanol (2 mL) and dried thoroughly *in vacuo*. Yield: 115 mg (67%). FeC₃₆H₈₆N₁₂O₈S₂: calc. C 58.83, H 7.58, N 14.70; found C 58.92, H 7.81, N 14.81%. IR (KBr, *inter alia*): 2920, 2950, 1651, 1602, 1591, 1489, 1455, 1241, 1159, 1075, 1040, 789, 747, 725, 712, 597. ESI-MS (pos.): m/z = 837.3392 [Fe(adpt)₂(C₁₆SO₃)]⁺, 599.2462 [Fe(adpt)(C₁₆SO₃)]⁺. UV/Vis/NIR (CH₃OH): λ_{max}/nm 480 (ε = 3040 L mol⁻¹ cm⁻¹), 1120 (45 L mol⁻¹ cm⁻¹).

[Fe^{II}(pdppt)₂(C₁₆SO₃)₂]

[Fe^{II}(OH)₂(C₁₆SO₃)₂] (70 mg, 0.10 mmol) and **pdppt** (58 mg, 0.20 mmol) were placed in a sample tube. Methanol (5 mL) was added, which caused the white powders to dissolve to form a clear, dark red solution within 5 minutes. This was stirred at room temperature, open to the air for an hour and then subjected to diethyl ether vapour diffusion which yielded fluffy, pale orange microcrystals. These were isolated by filtration, washed with 10 mL further diethyl ether, and then dried *in vacuo*. Yield = 67 mg (54%). FeC₆₄H₉₀N₁₂O₆S₂: calc. C 61.82, H 7.30, N 13.52; found C 61.74, H 7.58, N 13.51%. IR (KBr, *inter alia*): 2919, 2850, 1607, 1585, 1469, 1451, 1238, 1149, 1032, 1014, 797, 731, 615. ESI-MS (pos.): m/z = 937.3823 [Fe(pdppt)₂(C₁₆SO₃)]⁺, 599.2216 [Fe(pdppt)(C₁₆SO₃)]⁺. UV/Vis/NIR (CH₃OH): λ_{max}/nm 471 (ε = 445 L mol⁻¹ cm⁻¹), 1113 (ε = 64 L mol⁻¹ cm⁻¹).

[Co^{II}(adpt)₂(CH₃OH)₂](C₁₆SO₃)₂·H₂O

[Co^{II}(OH)₂(C₁₆SO₃)₂] (106 mg, 0.15 mmol) and **adpt** (71 mg, 0.30 mmol) were placed in a sample tube. Methanol (8 mL) was added, which caused the white powders to dissolve to form pale orange suspension. This was stirred at room temperature, open to the air for two hours. After this time, it was warmed, causing all material to dissolve to give a clear, pale orange solution. This was left to slowly evaporate, giving large pale orange block-like crystals. These were isolated by filtration, washed with ice-cold methanol (2 mL) and dried thoroughly *in vacuo*. Yield: 143 mg (77%). CoC₃₈H₉₄N₁₂O₈S₂·H₂O: calc. C 56.70, H 7.88, N 13.68; found C 56.86, H 8.16, N 13.63%. ESI-MS (pos.): m/z = 840.3534 [Co(adpt)₂(C₁₆SO₃)]⁺. IR (KBr, *inter alia*): 3415, 3234, 2917, 2849, 1641, 1605, 1591, 1572, 1461, 1428, 1297, 1256, 1233, 1205, 1170, 1046, 791, 758, 721, 702, 601. UV/Vis/NIR (CH₃OH): λ_{max}/nm 460 (ε = 46 L mol⁻¹ cm⁻¹).

[Co^{II}(pdppt)₂(CH₃OH)₂](C₁₆SO₃)₂·0.5CH₃OH

[Co^{II}(OH)₂(C₁₆SO₃)₂] (106 mg, 0.15 mmol) and **pdppt** (86 mg, 0.30 mmol) were placed in a sample tube. Methanol (8 mL) was added, which caused the white powders to dissolve to form a pale orange solution. This was stirred at room temperature, open to the air for two hours and then left to slowly evaporate, giving pale orange microcrystals. These were isolated by filtration, washed with ice-cold methanol (2 mL), and then dried *in vacuo*. Yield: 136 mg (68%). CoC₆₈H₉₈N₁₂O₈S₂·0.5CH₃OH: calc. C 60.21, H 7.60, N 12.67; found C 59.83, H 7.57, N 12.95%. ESI-MS (pos.): m/z = 1268.5760 [Co(pdppt)₂(C₁₆SO₃)₂]⁺, 940.3853 [Co(pdppt)(C₁₆SO₃)]⁺, 652.2664 [Co(pdppt)(C₁₆SO₃)]⁺. IR (KBr, *inter alia*): 2919, 2850, 1589, 1483, 1455, 1430, 1210, 1172, 1044, 1016, 985, 790, 738, 704. UV/Vis/NIR (CH₃OH): λ_{max}/nm : 460 (ε = 34 L mol⁻¹ cm⁻¹).

Table 1. Crystal structure determination details for the complexes [Fe^{II}(adpt)₂(C₁₆SO₃)₂] and [Co^{II}(adpt)₂(CH₃OH)₂](C₁₆SO₃)₂·1.33(CH₃OH).

	[Fe ^{II} (adpt) ₂ (C ₁₆ SO ₃) ₂]	[Co ^{II} (adpt) ₂ (CH ₃ OH) ₂](C ₁₆ SO ₃) ₂ ·1.33(CH ₃ OH)
Empirical formula	C ₅₆ H ₈₆ N ₁₂ O ₈ S ₂ Fe	C _{59.33} H _{99.33} N ₁₂ O _{9.33} S ₂ Co
M _r	1143.34	1253.22
Crystal system	Triclinic	Monoclinic
Space group	P-1	P2 ₁ /c
a [Å]	10.0978(6)	25.467(6)
b [Å]	14.2697(10)	15.060(4)
c [Å]	22.0872(15)	26.051(7)
α [°]	102.047(3)	90
β [°]	97.982(3)	97.714(12)
γ [°]	104.035(3)	90
V [Å ³]	2958.8(3)	9901(4)
Z	2	6
ρ _{calcd} [g/cm ³]	1.283	1.261
μ [mm ⁻¹]	0.384	0.385
F(000)	1224	4038
Crystal size [mm]	0.50 x 0.25 x 0.02	0.60 x 0.42 x 0.40
θ range for data collection [°]	1.52 to 26.38	2.32 to 26.65
Reflections collected	62470	234885
Independent reflections	12032	20632
R(int)	0.0627	0.0628
Max. and min. transmission	1.000 and 0.811	1.000 and 0.8777
Data / restraints / parameters	12032 / 696 / 0	20632 / 1140 / 0
Goof (F ²)	1.117	1.025
R ₁ [I > 2 σ (I)]	0.0659	0.0372
wR ₂ [all data]	0.1552	0.1096

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Notes and references

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- † Electronic Supplementary Information (ESI) available: Scheme 1, Figures S1–S4, Tables S1–S5. CCDC reference numbers 741107 & 741108. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/
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Table of Contents entry:

[Fe^{II}(**Rdpt**)₂(C₁₆SO₃)₂] and [Co^{II}(**Rdpt**)₂(CH₃OH)₂](C₁₆SO₃)₂, where **R** = amino or pyrrolyl and **dpt** is 3,5-bis(2-pyridyl)-1,2,4-triazole, are reported. A wide range of solution, and Langmuir air-water interface, studies of the iron(II) complexes are consistent with the presence of more than one species in solution.

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