Towards Langmuir–Blodgett films of magnetically interesting materials: solution equilibria in amphiphilic iron(II) complexes of a triazole-containing ligand†

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As a first step towards amphiphilic spin crossover (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), $[Fe^{II}(OH_2)_2(C_{16}SO_3)_2]$ and $[Co^{II}(OH_2)_2(C_{16}SO_3)_2]$ have been prepared and reacted with the triazole-containing ligands **adpt** and **pldpt** ($C_{16}SO_3$ = 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, two HS complexes of the form $[Fe^{II}(\mathbf{Rdpt})_2(C_{16}SO_3)_2]$ and two of the form $[Co^{II}(\mathbf{Rdpt})_2(CH_3OH)_2](C_{16}SO_3)_2$ are obtained, even when a six-fold excess of 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 $[Fe^{II}(\mathbf{Rdpt})_2(C_{16}SO_3)_2]$ and the dicationic low-spin *tris* form $[Fe^{II}(\mathbf{Rdpt})_3](C_{16}SO_3)_2$. 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 $[Fe^{II}(\mathbf{Rdpt})_3](C_{16}SO_3)_2$ form by adding additional ligand to the solution. The X-ray crystal structures of $[Fe^{II}(\mathbf{adpt})_2(C_{16}SO_3)_2]$ and $[Co^{II}(\mathbf{adpt})_2(CH_3OH)_2](C_{16}SO_3)_2 \cdot 1.33CH_3OH$ are presented. $[Fe^{II}(\mathbf{adpt})_2(C_{16}SO_3)_2]$ has a 2D bilayer structure with alternating layers of polar $Fe(\mathbf{adpt})_2$ centres, and hydrophobic alkyl chains. The complex cations in $[Co^{II}(\mathbf{adpt})_2(CH_3OH)_2](C_{16}SO_3)_2 \cdot 1.33CH_3OH$ form 1-D columns in the solid state. The capacity of the amphiphilic complexes $[Fe^{II}(\mathbf{pldpt})_2(C_{16}SO_3)_2]$ and $[Fe^{II}(\mathbf{adpt})_2(C_{16}SO_3)_2]$ 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),[2–8] 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.[9,10] 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.*[11] recently assembled $[Fe(pyrazine)(Pt(CN)_4)]$ on a gold surface, and observed a hysteretic SCO event, centred around room temperature. We also recently described a major improvement in the cooperativity of an iron(III) complex through self-assembly in solution.[12]

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 $\{[Fe(4R\text{-}trz)_3]X_2\}_n$, where 4R-trz is a 1,2,4-triazole moiety with a hydrophobic substituent at N^4 of the triazole ring,[13,14] or discrete complexes of the form $[FeL_2(NCS)_2]$, where L represents either phenanthroline or 2,2′-bipyridine groups that have been modified to contain long alkyl chains.[15–18,19]

Recently, Aida *et al.*[20] reported the preparation of gels of the form $[Fe(4R\text{-}trz)_3](C_nSO_3)_2$, where C_nSO_3 represents the sulfonate anion 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 approach 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.*,[21] and more recently by Kimizuka *et al.*[22] 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, $[Fe^{II}(OH_2)_2(C_{16}SO_3)_2]$, that Aida *et al.*[20] reported can be

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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 $[Fe^{II}(OH_2)_2(C_{16}SO_3)_2]$ by a slight modification of the method described by Aida et al.,[20] and extended this to prepare the analogous cobalt compound, $[Co^{II}(OH_2)_2(C_{16}SO_3)_2]$. We have reacted these two 'long tailed anion' reagents with two dipyridyltriazole-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**) (Fig. 1), as these two ligands are readily prepared and have previously given iron(II) complexes that show SCO behaviour.[23–33]
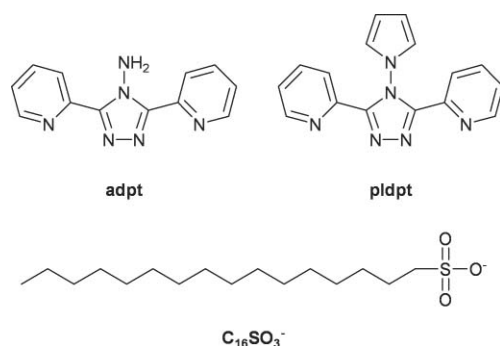

Fig. 1 Ligands and counter ion used in this study.

Results and discussion

Synthesis

The ligands **adpt** and **pldpt** (Fig. 1) were prepared in two and three steps, respectively, from commercially available precursors, as previously described (Scheme S1†).[34–36] We used a modification of Aida et al.'s procedure[20] to prepare the starting material, $[Fe^{II}(OH_2)_2(C_{16}SO_3)_2]$. 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, $[Fe^{II}(OH_2)_2(C_{16}SO_3)_2]$, 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 $[Fe^{II}(OH_2)_2(C_{16}SO_3)_2]$ 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 $[Co^{II}(OH_2)_2(C_{16}SO_3)_2]$; again, in analytically pure form and essentially quantitative yield (99%).

Regardless of whether two, three or six equivalents of **Rdpt** ligand were reacted with one equivalent of $[M^{II}(OH_2)_2(C_{16}SO_3)_2]$ (M = Fe or Co) in methanol at room temperature, 2 : 1 **Rdpt** : M products were isolated, not the originally hoped for $[M(Rdpt)_3](C_{16}SO_3)_2$ complexes (for detailed discussion see ESI†). The failure of even the 6 : 1 **Rdpt** : M reactions to allow isolation of solid samples of $[M(Rdpt)_3](C_{16}SO_3)_2$ species is remarkable, highlighting once again that the nature of the product isolated from reactions of these bidentate **Rdpt** ligands with first row transition metal ions is not controlled simply by reaction stoichiometry.[32,34,37] Attempts to carry out the reactions in different solvents were thwarted by the poor solubility of $[Fe^{II}(OH_2)_2(C_{16}SO_3)_2]$ in solvents other than methanol and water, and the poor solubility of the ligands in water.

In the case of iron(II), either subjecting the dark red reaction solution to diethyl ether vapour diffusion or allowing it to slowly evaporate gave analytically pure $[Fe(Rdpt)_2(C_{16}SO_3)_2]$, as pale orange microcrystals in reasonable yields (67% for **Rdpt** = **adpt**, 54% for **Rdpt** = **pldpt**). In the case of cobalt(II), the pale orange reaction solution gave $[Co^{II}(Rdpt)_2(CH_3OH)_2](C_{16}SO_3)_2 \cdot solvent$, as analytically pure orange microcrystals in good yields (77%, solvent = H_2O for **adpt**, 68%, solvent = $0.5CH_3OH$ for **pldpt**).

For all four complexes a peak was observed in the ESI MS spectrum corresponding to $[M(Rdpt)_2(C_{16}SO_3)]^+$. Consistent with the pale orange colour of all four of these complexes, the magnetic moments indicate that all of them exist in the high spin (HS) form in the solid state at room temperature.

Solution equilibria

Both $[Fe^{II}(adpt)_2(C_{16}SO_3)_2]$ and $[Fe^{II}(pldpt)_2(C_{16}SO_3)_2]$ exist as pale orange solids with μ_{eff} = 5.3 and 5.5 BM, respectively, 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 $[Fe^{II}(adpt)_2(C_{16}SO_3)_2]$ 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 $[Fe^{II}(adpt)_3](BF_4)_2$ and $[Fe^{II}(pldpt)_3](BF_4)_2$, which are LS at room temperature, and are rich red colours.[32] 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, $[Fe^{II}(Rdpt)_3](C_{16}SO_3)_2$ and the neutral HS bis complex $[Fe^{II}(Rdpt)_2(C_{16}SO_3)_2]$. Non-polar solvents presumably lead to stabilisation of the neutral (HS) species containing coordinated anions, while the addition of a more polar solvent stabilises the positively charged (LS) cationic species.

All of our studies with these potentially bis-bidentate **Rdpt** ligands and iron(II) have been considerably complicated by similar solution equilibria.[32,37]

UV/Vis/NIR spectroscopy

To investigate this further, methanol and dichloromethane solutions of $[Fe^{II}(OH_2)_2(C_{16}SO_3)_2]$, with various amounts of **Rdpt** ligand, were investigated between 400 nm and about 1200 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 (Fig. 2, Fig. S1 & S2†).
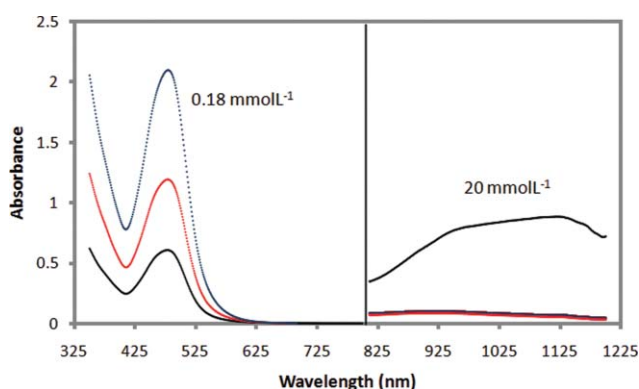

Fig. 2 UV/Vis/NIR spectra in MeOH for $[Fe^{II}(OH_2)_2(C_{16}SO_3)_2]$: **adpt** in; (black) 1 : 2 ratio, (red) 1 : 3 ratio, (dark blue) 1 : 6 ratio. Spectra were obtained on solutions of $[Fe]_{total}$ of 0.18 mmol L^{-1} (LHS) and 20 mmol L^{-1} (RHS).

Due to the probable existence of a mixture of solution species, extinction coefficients cannot be calculated reliably per complex, hence they are provided per Fe(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 ($\varepsilon = 3040$ L mol^{-1} cm^{-1}) is 70 times more intense than the band at 1119 nm ($\varepsilon = 45$ L mol^{-1} cm^{-1}). Changing this Fe(II) : **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 ($\varepsilon = 445$ L mol^{-1} cm^{-1}), was only 7 times more intense than the lower energy band at 1113 nm ($\varepsilon = 64$ L mol^{-1} 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$_2$Cl$_2$, but the low solubility only allowed observation of the more intense higher energy band (concentrations of 20 mmol L^{-1} were necessary to observe the longer wavelength signal in methanol; the complex does not have this great a solubility in CH$_2$Cl$_2$). The ~480 nm band decreases in intensity when switching from methanol to CH$_2$Cl$_2$ (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 $[Fe(\textbf{Rdpt})_3]^{2+}$ species, simultaneously reducing the intensity of the band at ~1100 nm arising from the HS $[Fe(\textbf{Rdpt})_2(C_{16}SO_3)_2]$ species.

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

Solid state and solution IR spectroscopy

The solid state IR spectrum of $[Fe^{II}(OH_2)_2(C_{16}SO_3)_2]$ 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 $[Fe^{II}(\textbf{adpt})_2(C_{16}SO_3)_2]$ and $[Fe^{II}(\textbf{pldpt})_2(C_{16}SO_3)_2]$ show this band at 1159 and 1149 cm^{-1} respectively (similar to the 1145 cm^{-1} band observed for $[Cu^{II}(OH_2)_2(C_{16}SO_3)_2]$,[38] although different to Aida *et al.*, who report this band at 1196 cm^{-1} in $[Fe^{II}(OH_2)_2(C_{16}SO_3)_2]$[20]). The solid state IR spectra of $[Co^{II}(\textbf{adpt})_2(CH_3OH)](C_{16}SO_3)_2$ and $[Co^{II}(\textbf{pldpt})_2(CH_3OH)_2]$ $(C_{16}SO_3)_2$ 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$_2$Cl$_2$ and 9 : 1 CH$_2$Cl$_2$/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 $[Fe^{II}(\textbf{adpt})_2(C_{16}SO_3)_2]$ or $[Fe^{II}(\textbf{pldpt})_2(C_{16}SO_3)_2]$ have high solubility in CH$_2$Cl$_2$ or 9 : 1 CH$_2$Cl$_2$/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 $[Fe^{II}(OH_2)_2(C_{16}SO_3)_2]$ and two equivalents of **pldpt** in CH$_2$Cl$_2$ shows the asymmetric S=O stretch at 1150 cm^{-1}– the same frequency as observed in the solid state spectrum of $[Fe^{II}(\textbf{pldpt})_2(C_{16}SO_3)_2]$, within the accuracy of our instrument. A very weak band appears to be present at ~1190 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 $[Fe^{II}(\textbf{pldpt})_2(C_{16}SO_3)_2]$ form of the complex is the major form of the complex in the non-polar solvent CH$_2$Cl$_2$. In contrast, the spectrum of one equivalent of $[Fe^{II}(OH_2)_2(C_{16}SO_3)_2]$ and two equivalents of **pldpt** in 9 : 1 CH$_2$Cl$_2$/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 $\{[Fe(4R\text{-trz})_3](C_{16}SO_3)_2\}_\infty$–these were observed between 1207 and 1213 cm^{-1}, depending on the spin state of the iron(II) complex.[20] Adding an extra equivalent of ligand does not cause this band to move, suggesting the $[Fe^{II}(\textbf{Rdpt})_3]^{2+}$ species is not involved in any equilibria in this solvent mixture.

Unfortunately, the solubility of $[Fe^{II}(OH_2)_2(C_{16}SO_3)_2]$/**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 $[Fe^{II}(OH_2)_2(C_{16}SO_3)_2]$ and **adpt** in 9 : 1 CH$_2$Cl$_2$/methanol are very similar to those observed for the analogous **pldpt**-containing mixtures.

To summarise: in straight CH_2Cl_2, mixtures of $[Fe^{II}(OH_2)_2(C_{16}SO_3)_2]$ and **pldpt** seem to exist predominantly as the neutral form of the complex, *i.e.* $[Fe^{II}(pldpt)_2(C_{16}SO_3)_2]$. 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.[39] All of the spectra were recorded in d_4-methanol spiked with dichloromethane, so that the shift in the proton signal of the dichloromethane could be monitored (unlike methanol, dichloromethane should not coordinate).

The dichloromethane proton signal in a 15 mmol L^{-1} solution of $[Fe^{II}(adpt)_2(C_{16}SO_3)_2]$ shifted downfield (0.333 ppm, $\Delta f = 133$ Hz) relative to a capillary of the blank solvent mixture, corresponding to a magnetic susceptibility of about 5.3 B.M. per iron(II) centre (see experimental). This is consistent with the majority of the solution being in the HS $[Fe^{II}(adpt)_2(C_{16}SO_3)_2]$ form, possibly with a small contribution from a LS $[Fe^{II}(adpt)_3]^{2+}$ (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 (0.021 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 $[Fe^{II}(adpt)_3]^{2+}$ form when the Fe(II) : **adpt** ratio is 1 : 3.

In the case of $[Fe^{II}(pldpt)_2(C_{16}SO_3)_2]$, the dichloromethane proton signal of a 16 mmol L^{-1} solution of $[Fe^{II}(pldpt)_2(C_{16}SO_3)_2]$ shifted downfield (0.462 ppm, $\Delta f = 185$ Hz) relative to a capillary of blank solvent, corresponding to a magnetic susceptibility of about 5.7 B.M. per iron(II) centre. Adding an extra equivalent of ligand caused a smaller shift of the dichloromethane proton signal downfield (0.067 ppm, $\Delta f = 27$ Hz) relative to the blank solvent, corresponding to a magnetic susceptibility of about 1.7 B.M. indicating a change by some, but not all, of the HS $[Fe^{II}(pldpt)_2(C_{16}SO_3)_2]$ molecules to the LS $[Fe^{II}(pldpt)_3]^{2+}$. This is consistent with UV-Vis studies, which indeed show conversion of $[Fe^{II}(pldpt)_2(C_{16}SO_3)_2]$ to $[Fe^{II}(pldpt)_3]^{2+}$, but to a lesser extent than when **adpt** is used.

Behaviour of the complexes at the air–water interface

The capacity of the amphiphilic complexes $[Fe^{II}(pldpt)_2(C_{16}SO_3)_2]$ and $[Fe^{II}(adpt)_2(C_{16}SO_3)_2]$ to self-assemble has been probed at the air–water interface using Langmuir techniques.[40,41] 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 (Fig. 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 $[Fe^{II}(pldpt)_2(C_{16}SO_3)_2]$, $[Fe^{II}(adpt)_2(C_{16}SO_3)_2]$, or the *aqua* complex $[Fe^{II}(H_2O)_6(C_{16}SO_3)_2]$ were employed for film fabrication (Fig. 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 Å^2 per Fe(sulfonate)$_2$ unit. Such an area is far too small for an amphiphile comprising two alkyl chains (*cf.* 22 Å^2/molecule determined for a single alkyl chain in behenic acid[42]). 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.[43] Similar instability of iron(II) triazole complexes at the air–water interface has been noted by Kahn and coworkers.[14] Ligand modifications, especially the use of polydentate scaffolds, may lead to improved stability properties.[15–18]
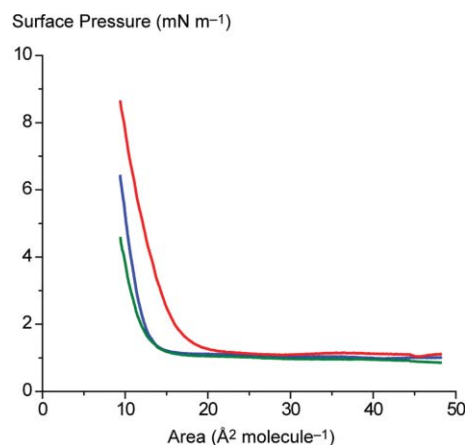

Fig. 3 Representative pressure-area isotherms for Langmuir films prepared from $[Fe^{II}(pldpt)_2(C_{16}SO_3)_2]$ (green), $[Fe^{II}(adpt)_2(C_{16}SO_3)_2]$ (red), and $[Fe^{II}(H_2O)_6(C_{16}SO_3)_2]$ (blue), indicating identical molecular areas for all films.

X-ray crystallography

Single crystals of $[Fe^{II}(adpt)_2(C_{16}SO_3)_2]$ 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 (Fig. 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) and consistent with the observed magnetic moment. 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
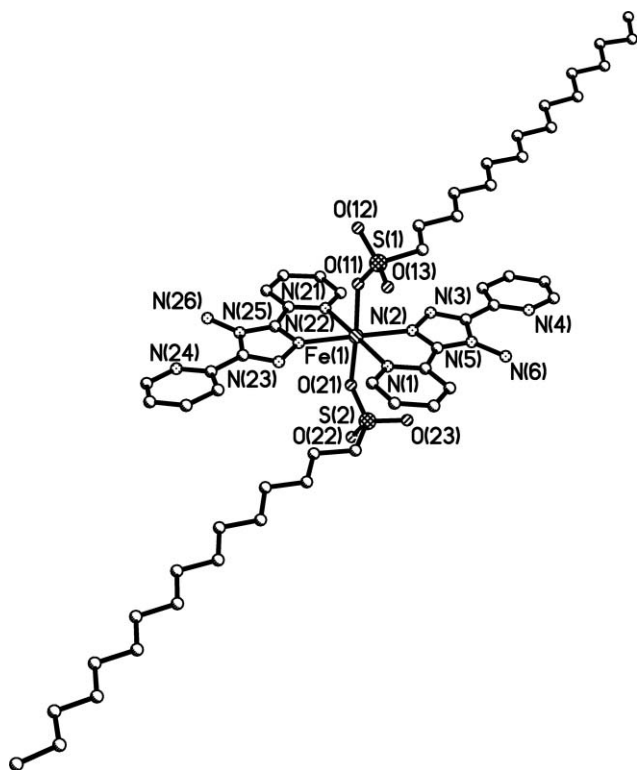
Fig. 4 Perspective view of [Fe^{II}(**adpt**)$_2$(C$_{16}$SO$_3$)$_2$]. Hydrogen atoms omitted for clarity.

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.

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°] (Fig. 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°, Fig. S5†]. Moderate offset parallel π–π stacking (Fig. 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 (Fig. 5 & S7†) to give the complex a bilayered structure.

Single crystals of [Co^{II}(**adpt**)$_2$(CH$_3$OH)$_2$](C$_{16}$SO$_3$)$_2$·1.33CH$_3$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 (Fig. 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} and consistent with the observed magnetic moment. Very small twists are seen between the coordinated pyridine and
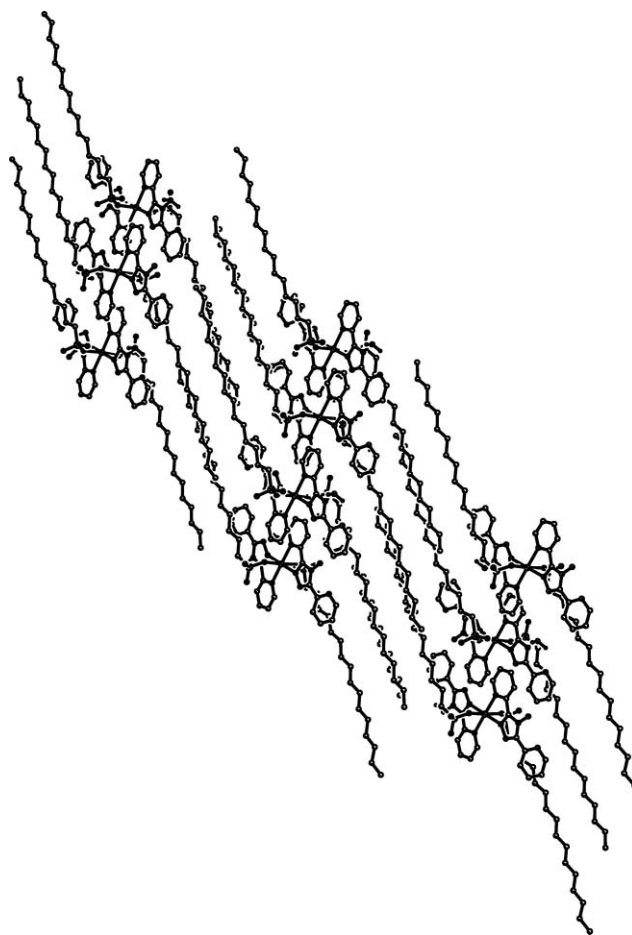

Fig. 5 View of packing down the *a*-axis of [Fe^{II}(**adpt**)$_2$(C$_{16}$SO$_3$)$_2$]. Hydrogen atoms omitted for clarity.

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 Co(**adpt**)$_2$ core very close to planar.

Very strong hydrogen bonds are seen between the coordinated methanol groups and sulfonate oxygens [O–H···O = 2.5831(19)-2.6144(19) Å, <O–H···O = 167.9-177.5°] (Fig. 6), with weaker hydrogen bonds between the methanol solvates and other sulfonate oxygen atoms [O–H···O = 2.756(2)-2.778(2) Å, <O–H···O = 156.7-163.0°] (Fig. S8†).

One proton from each amino group hydrogen bonds to the non-coordinated pyridine nitrogen atom from the same ligand strand [N–H···N = 2.861(2)-2.887(2), <N–H···N = 134.3 to 137.6°], with the other hydrogen-bonding to a sulfonate group [N–H···N = 2.849(2)-2.903(2), <N–H···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···O = 2.8878(17)-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 Co(**adpt**)$_2$ planes perpendicular to the adjacent column (Fig. S9†). No significant π–π stacking is observed. For full details of the supramolecular interactions in both complexes see Tables S2–S4†.
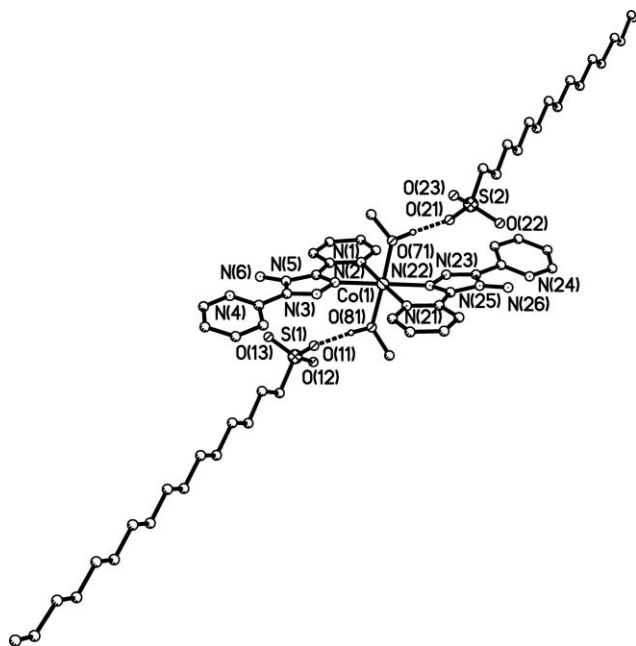
Fig. 6 Perspective view of $[Co^{II}(\mathbf{adpt})_2(CH_3OH)_2](C_{16}SO_3)_2 \cdot 1.33CH_3OH$. Lattice methanol molecules and hydrogen atoms, except the methanol OH protons, are omitted for clarity.

Conclusions

Herein we provide details of a refined, high yielding (96-99%) synthesis of pure $[Fe(OH_2)_2(C_{16}SO_3)_2]$ and $[Co(OH_2)_2(C_{16}SO_3)_2]$. 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 $[M^{II}(\mathbf{Rdpt})_2X_2]^{n+}$, where M^{II} 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 $[M(\mathbf{Rdpt})_2X_2]^{n+}$ 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 $[Fe(\mathbf{Rdpt})_3]^{2+}$. When R = NH_2 (**adpt**), the conversion to the *tris* form is virtually complete and is accompanied by a substantial 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,[32] 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 1:6 metal:ligand ratio was used in the reactions, were pure $[M(\mathbf{Rdpt})_2X_2]^{n+}$, not $[M(\mathbf{Rdpt})_3]^{2+}$, complexes. This contrasts with

the results of our studies of $[Fe(\mathbf{Rdpt})_3]^{2+}$ complexes with BF_4 counter ions,[32] but is consistent with our general experience with these **Rdpt** ligands - that the nature of the solid product obtained is not at all easily controlled, as it is influenced by many factors,[34,37] and choice of reaction stoichiometry alone is often not sufficient.

Pressure-area isotherms of Langmuir films of $[Fe(\mathbf{Rdpt})_2-(C_{16}SO_3)_2]$ (**R** = 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 focused 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 $[Fe^{II}_2(\mathbf{PMAT})_2](BF_4)_4$ of the *bis-terdentate* ligand **PMAT**, 4-amino-3,5-bis{[(2-pyridylmethyl) amino]methyl}-$4H$-1,2,4-triazole,[44–46]–*i.e.* $[Fe^{II}_2(\mathbf{PMAT})_2](C_{16}SO_3)_4$. 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. Room temperature magnetic moments were determined using a Johnson Matthey MSB-MK1 magnetic susceptibility balance.

Solution magnetic moments were measured by the Evan's method in a CD_3OD containing a trace amount of CH_2Cl_2, using CH_2Cl_2 (which unlike methanol should not coordinate) as the chemical shift reference,[39] in a double walled NMR tube on a 400 MHz Varian INOVA-400 spectrometer at 25 °C. The concentrations employed and observed shifts of the methylene signal are given in the text. All calculations, including magnetic moment, employed the concentration of iron(II) calculated from the amount of $[Fe(\mathbf{Rdpt})_2(C_{16}SO_3)_2]$ dissolved in the volume of CD_3OD used, regardless of what iron(II) species or mixture of species resulted from the dissolution process and/or from subsequent addition of **Rdpt**, so are per iron(II).

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-Kα radiation (λ = 0.71073 Å) was used. Both data sets were corrected for absorption using SCALE.[47,48] The structures were solved using SHELXS-97.[49] Both structures were refined against F^2 using all data by full matrix least squares techniques with SHELXL-97.[49] All non-hydrogen atoms were modelled anisotropically. The amino protons were found in the map and their coordinates fixed. All other hydrogen atoms were inserted at calculated positions and rode on the atoms to which they are attached. All hydrogen atom isotropic thermal parameters were made equal to 1.2 times that of the attached non-hydrogen atom. Crystal structure determination details are summarized in Table 1. Neither structure contained any disorder.

Table 1 Crystal structure determination details for the complexes [Fe^{II}(adpt)$_2$(C$_{16}$SO$_3$)$_2$] and [Co^{II}(adpt)$_2$(CH$_3$OH)$_2$](C$_{16}$SO$_3$)$_2$·1.33(CH$_3$OH)

	[Fe^{II}(adpt)$_2$-(C$_{16}$SO$_3$)$_2$]	[Co^{II}(adpt)$_2$(CH$_3$OH)$_2$]-(C$_{16}$SO$_3$)$_2$
Empirical formula	C$_{56}$H$_{86}$N$_{12}$O$_6$-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	Monoclininc
Space group	$P\bar{1}$	$P2_1/c$
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_c/g cm^{-3}	1.283	1.261
μ/mm^{-1}	0.384	0.385
$F(000)$	1224	4038
Crystal size/mm	0.50 × 0.25 × 0.02	0.60 × 0.42 × 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 [$I > 2\sigma(I)$]	0.0659	0.0372
wR_2 [all data]	0.1552	0.1096

Adpt and **pldpt** were prepared by literature methods;[34–36] 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}(pldpt)$_2$(C$_{16}$SO$_3$)$_2$] and a 97 : 3 mixture of chloroform–MeOH for [Fe^{II}(adpt)$_2$(C$_{16}$SO$_3$)$_2$] and [Fe^{II}(H$_2$O)$_2$(C$_{16}$SO$_3$)$_2$]. 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 cm^2 min^{-1}) and the surface pressure was monitored using a platinum Wilhelmy plate.

[Fe^{II}(OH$_2$)$_2$(C$_{16}$SO$_3$)$_2$]

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%). FeC$_{32}$H$_{70}$O$_8$S$_2$: 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$_2$)$_2$(C$_{16}$SO$_3$)$_2$]$^+$, 379.1687 [Fe(OH$_2$)(C$_{16}$SO$_3$)]$^+$, 361.1677 = [Fe(C$_{16}$SO$_3$)]$^+$.

[Co^{II}(OH$_2$)$_2$(C$_{16}$SO$_3$)$_2$]

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%). CoC$_{32}$H$_{70}$O$_8$S$_2$: 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$_2$)$_2$(C$_{16}$SO$_3$)$_2$], 382.1699 [Co(OH$_2$)(C$_{16}$SO$_3$)]$^+$, 364.1699 [Co(C$_{16}$SO$_3$)]$^+$.

[Fe^{II}(adpt)$_2$(C$_{16}$SO$_3$)$_2$]

[Fe^{II}(OH$_2$)$_2$(C$_{16}$SO$_3$)$_2$ (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 h, 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%). FeC$_{56}$H$_{86}$N$_{12}$O$_6$S$_2$: 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**)$_2$(C$_{16}$SO$_3$)]$^+$, 599.2462 [Fe(**adpt**)(C$_{16}$SO$_3$)]$^+$. UV/Vis/NIR (CH$_3$OH): λ_{max}/nm 480 (ε = 3040 L mol(Fe)$^{-1}$ cm^{-1}), 1120 (45 L mol^{-1} cm^{-1}). μ_{eff} (solid) = 5.3 BM.

[Fe^{II}(pldpt)$_2$(C$_{16}$SO$_3$)$_2$]

[Fe^{II}(OH$_2$)$_2$(C$_{16}$SO$_3$)$_2$ (70 mg, 0.10 mmol) and **pldpt** (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 min. 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%). FeC$_{64}$H$_{90}$N$_{12}$O$_6$S$_2$: 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(**pldpt**)$_2$(C$_{16}$SO$_3$)]$^+$, 599.2216 [Fe(**pldpt**)(C$_{16}$SO$_3$)]$^+$. UV/Vis/NIR (CH$_3$OH): λ_{max}/nm 471 (ε = 445 L mol(Fe)$^{-1}$ cm^{-1}), 1113 (ε = 64 L mol^{-1} cm^{-1}). μ_{eff} (solid) = 5.5 BM.

[Co^{II}(adpt)$_2$(CH$_3$OH)$_2$](C$_{16}$SO$_3$)$_2$·H$_2$O

[Co^{II}(OH$_2$)$_2$(C$_{16}$SO$_3$)$_2$ (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%). CoC$_{58}$H$_{94}$N$_{12}$O$_8$S$_2$·H$_2$O: 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**)$_2$(C$_{16}$SO$_3$)]$^+$. 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 (CH$_3$OH): λ_{max}/nm 460 (ε = 46 L mol(Co)$^{-1}$ cm^{-1}). μ_{eff} (solid) = 5.0 BM.

[Co^{II}(pldpt)$_2$(CH$_3$OH)$_2$](C$_{16}$SO$_3$)$_2$·0.5CH$_3$OH

[Co^{II}(OH$_2$)$_2$(C$_{16}$SO$_3$)$_2$] (106 mg, 0.15 mmol) and **pldpt** (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%). CoC$_{68}$H$_{98}$N$_{12}$O$_8$S$_2$·0.5CH$_3$OH: 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(**pldpt**)$_2$(C$_{16}$SO$_3$)$_2$]Na$^+$, 940.3853 [Co(**pldpt**)$_2$(C$_{16}$SO$_3$)]$^+$, 652.2664 [Co(**pldpt**)(C$_{16}$SO$_3$)]$^+$. IR (KBr, *inter alia*): 2919, 2850, 1589, 1483, 1455, 1430, 1210, 1172, 1044, 1016, 985, 790, 738, 704. UV/Vis/NIR (CH$_3$OH): λ_{max}/nm: 460 (ε = 34 L mol(Co)$^{-1}$ cm^{-1}). μ_{eff} (solid) = 4.7 BM.

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