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Synthesis and Some First-Row Transition-Metal Complexes of the 1,2,4-Triazole-Based Bis(terdentate) Ligands TsPMAT and PMAT

Marco H. Klingele,[a] Boujemaa Moubaraki,[b] Keith S. Murray,[b] and Sally Brooker*[a]

Abstract: The employment of a strategy based on nucleophilic substitution, rather than Schiff base condensation, for the preparation of 1,2,4-triazole-based ligands has been investigated and has led to the synthesis of two new ligands, 4-amino-3,5-bis{[*N*-(2-pyridylmethyl)-*N*-(4-toluenesulfonyl)amino]-methyl}-4*H*-1,2,4-triazole (TsPMAT, **14**) and 4-amino-3,5-bis{[(2-pyridylmethyl)amino]methyl}-4*H*-1,2,4-triazole (PMAT, **15**). These are the first examples of bis(terdentate) ligands incorporating the 1,2,4-triazole unit. TsPMAT (**14**) forms a dinuclear 2:2 complex with $Co(BF_4)_2{\cdot}6H_2O$ even when reacted in a metal-to-ligand molar ratio of 2:1. Similarly, the reaction of PMAT (**15**) with $Mn(ClO_4)_2{\cdot}6H_2O$ or $M(BF_4)_2{\cdot}6H_2O$ (M = Fe, Co, Ni, Zn) in a ligand-to-metal molar ratio of 1:1 has afforded a series of complexes with the general formula $[M^{II}_2(PMAT)_2]X_4$. The metal centres in these complexes of TsPMAT (**14**) and PMAT (**15**) are encapsulated by two ligand molecules and doubly bridged by the N_2 units of the 1,2,4-triazole moieties, which gives rise to N_6 coordination spheres that are strongly distorted from octahedral, as evidenced by the X-ray crystal structure analyses of $[Co^{II}_2(TsPMAT)_2](BF_4)_4{\cdot}6MeCN$ (**24**·6MeCN) and $[Fe^{II}_2(PMAT)_2](BF_4)_4{\cdot}DMF$ (**27**·DMF). Studies of the magnetic properties of $[Co^{II}_2(TsPMAT)_2](BF_4)_4{\cdot}4H_2O$ (**24**·4H_2O), $[Mn^{II}_2(PMAT)_2](ClO_4)_4$ (**26**), and $[Co^{II}_2(PMAT)_2](BF_4)_4$ (**28**) have revealed weak antiferromagnetic coupling ($J = -3.3$, -0.16, and $-2.4\ cm^{-1}$, respectively) between the two metal centres in these complexes.

Keywords: bridging ligands · dinuclear complexes · magnetic properties · nucleophilic substitution · X-ray diffraction

Introduction

The incorporation of 3,6-pyridazinedicarbaldehyde (**1**) into Schiff base ligands has facilitated the isolation of a wide range of transition-metal complexes with intriguing electrochemical and magnetic properties,[1–19] including the first example of a cobalt complex to exhibit both magnetic exchange coupling and the spin-crossover phenomenon.[5,9] In light of this and with regard to the considerable recent interest in transition-metal complexes derived from 1,2,4-triazole-based ligands[15,20,21] that are known to be particularly suited to produce spin-crossover systems with iron(II) salts,[22–25] we decided to investigate the possibility of incorporating the 1,2,4-triazole moiety into novel acyclic and macrocyclic ligand systems capable of binding and bridging two metal ions.[26–31] Owing to its versatility and relative simplicity the Schiff base approach[32–36] was initially considered for the construction of the target 1,2,4-triazole-based ligands. This approach requires that the 1,2,4-triazole moiety forms a part of either the dicarbonyl head unit or the diamine lateral component. We focused our attention on the former option as a literature search revealed that five such 3,5-diacyl-1,2,4-triazole head units, compounds **2**–**6**, were known.[37–40] However, two of these head units, namely 1-(4-methoxybenzyl)-1*H*-1,2,4-triazole-3,5-dicarbaldehyde (**5**)[38,39] and 1-dodecyl-1*H*-1,2,4-triazole-3,5-dicarbaldehyde (**6**),[39] are unsuitable for our purposes as in both compounds one of the nitrogen atoms of the potentially metal ion bridging N_2 unit is blocked by the alkyl group. This left three potentially suitable head units, compounds **2**–**4**, of which dialdehyde **3** and diketone **4** are ionisable, due to the presence of an acidic proton on the 1,2,4-triazole ring, whereas diketone **2** is not. Metal-ion-templated condensation reactions of 3,5-dibenzoyl-4-phenyl-4*H*-1,2,4-triazole (**2**),[37] a sterically encumbered but very soluble diketone head unit, with a variety of amines were not found to be very promising.

[a] Dr. M. H. Klingele, Assoc. Prof. S. Brooker
Department of Chemistry, University of Otago
PO Box 56, Dunedin (New Zealand)
Fax: (+64) 3-479-7906
E-mail: sbrooker@alkali.otago.ac.nz

[b] Dr. B. Moubaraki, Prof. K. S. Murray
School of Chemistry, Building 23, Monash University
Clayton, Victoria 3800 (Australia)

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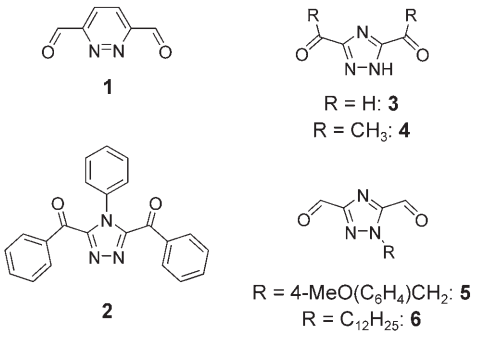
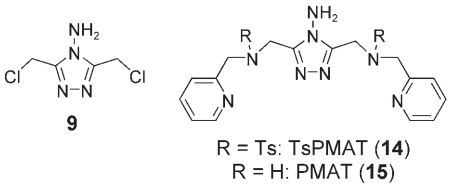
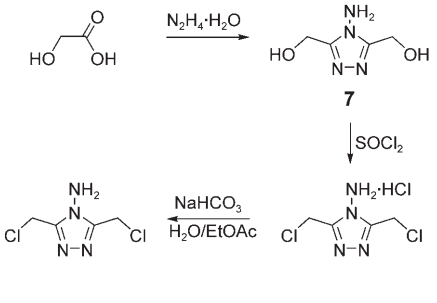


Torres and co-workers reported the synthesis of 1*H*-1,2,4-triazole-3,5-dicarbaldehyde (**3**) and 3,5-diacetyl-1*H*-1,2,4-triazole (**4**) in 1992[40] and the incorporation of these head units into Schiff base ligands was subsequently studied.[39,41–43] As they found that dialdehyde **3** was unsuitable for the preparation of such ligands due to its instability and its insolubility in all solvents other than water,[39] we initially concentrated our efforts on diketone **4**. Thus, we were recently able to prepare and structurally characterise the first dinuclear [2+2] macrocyclic complexes of any 1,2,4-triazole-derived ligand.[26–28] However, we found it difficult to isolate and purify these doubly 1,2,4-triazolate-bridged macrocyclic complexes and we concluded that diketone **4** was not an ideal head unit. Owing to the lack of any other more suitable 3,5-diacyl-1,2,4-triazoles, we decided to also investigate a strategy other than Schiff base chemistry for the construction of the desired metal-ion-bridging 1,2,4-triazole-based ligands, namely an approach based on nucleophilic substitution of a 1,2,4-triazole precursor that has suitable leaving groups within the substituents in the 3- and 5-positions. The known compound 4-amino-3,5-bis(chloromethyl)-4*H*-1,2,4-triazole (**9**)[44] was chosen for this purpose. In this paper we report the stepwise synthesis of two new ligands, 4-amino-3,5-bis{[*N*-(2-pyridylmethyl)-*N*-(4-toluenesulfonyl)amino]-methyl}-4*H*-1,2,4-triazole (TsPMAT, **14**) and 4-amino-3,5-bis{[(2-pyridylmethyl)amino]methyl}-4*H*-1,2,4-triazole (PMAT, **15**). To the best of our knowledge, these are the first examples of bis(terdentate) ligands incorporating a metal-ion-bridging 1,2,4-triazole unit. Kaden and co-workers[45] recently reported the synthesis of a related bis(quadridentate) ligand bearing two 1,3,7-triazacyclononane moieties as lateral units. A bis(terdentate)[46] and a mixed quadridentate–quinquedentate ligand[47] based on 2,5-disubstituted 1,3,4-oxadiazoles have also recently been reported. Attempts to extend the approach used for the synthesis of TsPMAT (**14**) and PMAT (**15**) to the preparation of other acyclic and macrocyclic ligands are also described. Employing PMAT (**15**), we were recently able to identify, for the first time by means of single-crystal X-ray diffraction, that the half-spin-crossover species of the doubly 1,2,4-triazole-bridged complex $[Fe^{II}_2(PMAT)_2](BF_4)_4$·DMF (**27**·DMF) is composed of discrete dinuclear high-spin/low-spin units.[31] Thus, we were able to confirm the conclusions drawn by Real, Gütlich, and co-workers[48,49] on the basis of magnetic and applied-field Mössbauer data on the pathway of the transition in their two-step spin-crossover systems. These results are in contrast to the recent results of Kaizaki and co-workers[50] who found a 1:1 mixture of high-spin/high-spin and low-spin/low-spin dinuclear units present at the half-spin-crossover plateau of the two-step transition in their pyrazolate-bridged system. Here, we detail the synthesis of complex **27**·DMF and some analogous first-row transition-metal complexes of PMAT (**15**), as well as reporting the results of our initial investigation of the coordination chemistry of TsPMAT (**14**).



Results and Discussion

Organic syntheses: The only method described in the literature for the preparation of the required 1,2,4-triazole precursor, 4-amino-4*H*-1,2,4-triazole-3,5-dimethanol (**7**), is the condensation of glycolic acid with hydrazine monohydrate (Scheme 1).[51–53] The original protocol by Adámek[51] starts with anhydrous glycolic acid and involves a rather complicated temperature programme. In a more recent modification of this synthesis by Haasnoot and co-workers,[52,53] the two reactants are simply heated together at 180 °C until water formation ceases. Both protocols were reviewed. We did not find it advantageous to follow Adámek's temperature programme, and our attempt using the procedure by Haasnoot and co-workers yielded an unidentified red glassy solid. It seemed to be crucial to maintain the reaction temperature below approximately 165 °C at all times and to use an excess (1.5 equivalents) of hydrazine monohydrate, as the same discoloured glassy solid was obtained when equimolar



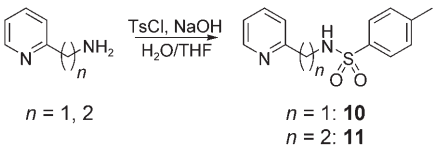
Scheme 1. Synthesis of 4-amino-3,5-bis(chloromethyl)-4*H*-1,2,4-triazole (**9**).

amounts of the reactants were used. Moreover, it was found that glycolic acid could be used in the form of the commercially available 70% aqueous solution instead of the much more expensive anhydrous material.

The synthesis of dialcohol **7** was carried out several times in exactly the same way. Interestingly, the crude products from these experiments varied considerably in composition. While in one case the crude product consisted of almost pure dialcohol **7**, other experiments gave only about 70% conversion, the major impurity being the intermediate glycolohydrazide. In the latter case prolonged heating did not result in further conversion unless a new portion of hydrazine monohydrate was added first. Regardless of the actual composition of the crude product, recrystallisation from water consistently gave yields of approximately 60% of analytically pure material. The use of water[51] for the recrystallisation proved to be preferable, as a very large volume of solvent was required when ethanol[52] was used. In addition, due to the high solubility of glycolohydrazide in water, the water-recrystallised product was of higher purity than the ethanol-recrystallised material. Therefore the yield of 60–65% obtained by Haasnoot and co-workers[52,53] seems more realistic than the 94% yield that Adámek[51] reported. Consistent with this, Kaden and co-workers[45] recently reported that they obtained a 68% yield of dialcohol **7** following Adámek's procedure.

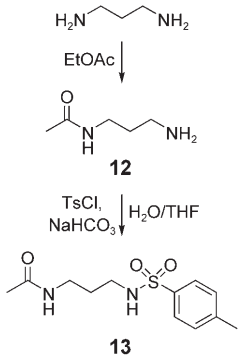
The conversion of dialcohol **7** into 4-amino-3,5-bis(chloromethyl)-4*H*-1,2,4-triazole monohydrochloride (**8**) was straightforward and proceeded smoothly in an excess of thionyl chloride at room temperature (Scheme 1).[54] The crude product was obtained in virtually quantitative yield as a yellowish solid after removal of the excess thionyl chloride in vacuo. Recrystallisation from ethanol afforded analytically pure material as colourless prisms in 76% yield. In an attempt to obtain dichloride **9** directly, without prior isolation and purification of hydrochloride **8**, the crude material was taken up in an excess of saturated aqueous sodium hydrogen carbonate.[44] However, only a low yield of dichloride **9** was obtained after exhaustive extraction with ethyl acetate. This was attributed to partial hydrolysis of dichloride **9** under the basic conditions. Careful neutralisation of hydrochloride **8** under heterogeneous conditions with one equivalent of sodium hydrogen carbonate in water/ethyl acetate gave pure dichloride **9** in 87% yield (Scheme 1). Attempts to recrystallise dichloride **9** from hot mixtures of ethyl acetate and cyclohexane led to decomposition and the formation of a colourless insoluble material, which is thought to be a polymer formed by the intermolecular nucleophilic displacement of the chlorides by 4-amino groups. Dichloride **9** degraded within a few days when stored at room temperature and exposed to light, again appearing to form a polymeric material. However, it should be pointed out that others have successfully carried out nucleophilic substitutions on dichloride **9**, even at high temperatures, and have made no comments on its instability.[44,55,56]

The reaction of free amines with alkyl halides is usually difficult to control and often leads to a mixture of multiply alkylated amines and ammonium salts. To couple the 1,2,4-triazole head unit with the lateral units in a controlled manner we decided to use sulfonamide derivatives of the amines rather than the free amines themselves. Thus, to prepare acyclic ligands, we treated commercially available 2-(aminomethyl)pyridine and 2-(2-aminoethyl)pyridine with 4-toluenesulfonyl chloride in water/tetrahydrofuran in the presence of sodium hydroxide (Scheme 2), a slight modification of the procedure reported by Newkome and co-workers.[57] This method afforded good yields of the desired products. Interestingly, we found that *N*-(2-pyridylmethyl)-4-toluenesulfonamide (**10**), unlike its homologue *N*-[2-(2-pyridyl)ethyl]-4-toluenesulfonamide (**11**), crystallises with half a molecule of water in the lattice. This fact had not been reported when this project was launched, even though sulfonamide **10** had been prepared and used by a number of authors over the years. However, recently the single-crystal X-ray structure analysis of sulfonamide **10**·0.5 H_2O was published by Sousa and co-workers,[58] thus confirming our observation.



Scheme 2. Synthesis of *N*-(2-pyridylmethyl)-4-toluenesulfonamide (**10**) and *N*-[2-(2-pyridyl)ethyl]-4-toluenesulfonamide (**11**).

For the preparation of macrocyclic ligands, a sulfonamide bearing a second functional group to allow the controlled stepwise construction of the target macrocycle was required. We chose *N*-{3-[(4-toluenesulfonyl)amino]propyl}acetamide (**13**)[59,60] (Scheme 3) for this purpose as, after coupling with the 1,2,4-triazole head unit, hydrolysis of its acetamide group could provide the required functionality for ring-closure. Initially we followed the procedure for the preparation of sulfonamide **13** reported by Hesse and co-workers,[59,60] but found it necessary to modify the reported workup procedure. The product obtained by the resulting extractive workup of the reaction mixture was contaminated with considerable amounts of byproducts and proved to be difficult to purify. Therefore we used a different approach to prepare sulfonamide **13** (Scheme 3).

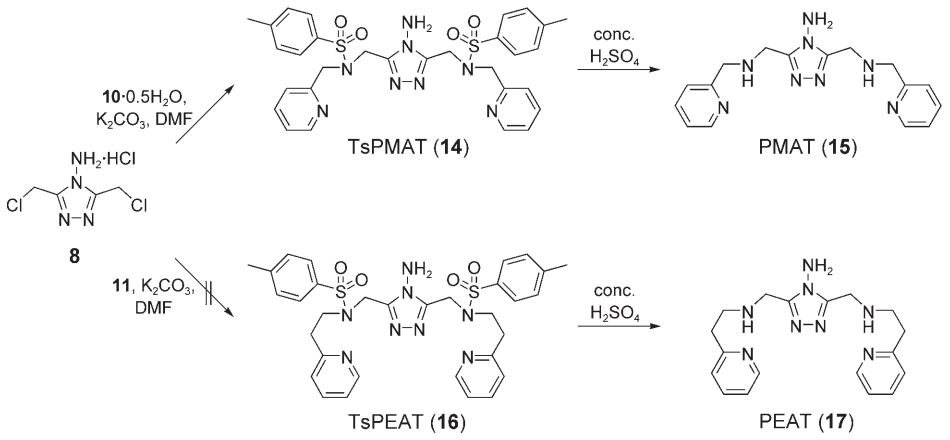


Scheme 3. Synthesis of *N*-{3-[(4-toluenesulfonyl)amino]propyl}acetamide (**13**).

While the selective monoacylation of symmetrical diamines is not trivial,[61,62] *N*-(3-aminopropyl)acetamide (**12**) can be readily obtained by using ethyl acetate as the acetyla-

tion agent as described by Aspinall.[63,64] Thus, we treated a threefold excess of 1,3-diaminopropane with ethyl acetate at room temperature for five days to give acetamide **12** in 87% yield and good purity.[65] Subsequent reaction with 4-toluenesulfonyl chloride gave NMR- and TLC-clean sulfonamide **13** in 92% yield (Scheme 3). This new approach simplified the synthesis and increased the yield of sulfonamide **13** significantly. The crude material was pure enough for subsequent reactions. Recrystallisation from ethyl acetate[60] was impractical due to the low solubility of the material in this solvent. A number of other solvents were tested of which 1,4-dioxane proved to be the best. However, only about 30–45% of sulfonamide **13** was recovered and the crystallisation process was very slow.

With the required 1,2,4-triazole (**8** or **9**) and sulfonamide components (**10**, **11** or **13**) in hand, we investigated their coupling reactions. Owing to the instability of dichloride **9**, the usefulness of hydrochloride **8** was explored. Initially the acyclic ligands TsPMAT (**14**) and PMAT (**15**) were targeted (Scheme 4). After 24 h under reflux, we could not detect any product when the reaction of hydrochloride **8** with sulfonamide **10**·0.5 H_2O in the presence of potassium carbonate was carried out in acetonitrile. This was attributed to the insolubility of hydrochloride **8** in this solvent. Carrying out the reaction at 60 °C in *N*,*N*-dimethylformamide, in which hydrochloride **8** is readily soluble, we obtained TsPMAT (**14**) as a colourless powder in 60% yield after workup. Removal of the 4-toluenesulfonyl group was achieved by heating a solution of TsPMAT (**14**) in concentrated sulfuric acid at 100 °C for 8 h. Thus, PMAT (**15**) was isolated as a yellowish oil in virtually quantitative yield (Scheme 4).



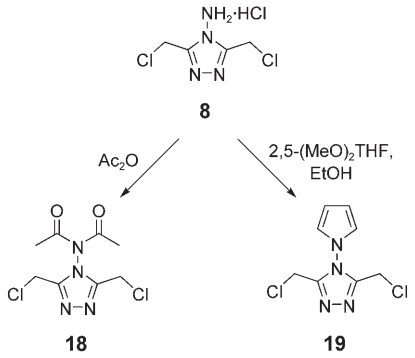
Scheme 4. Synthesis of 4-amino-3,5-bis{[*N*-(2-pyridylmethyl)-*N*-(4-toluenesulfonyl)amino]methyl}-4*H*-1,2,4-triazole (TsPMAT, **14**) and 4-amino-3,5-bis{[(2-pyridylmethyl)amino]methyl}-4*H*-1,2,4-triazole (PMAT, **15**) and attempted synthesis of 4-amino-3,5-bis({*N*-[2-(2-pyridyl)ethyl]-*N*-(4-toluenesulfonyl)amino}methyl)-4*H*-1,2,4-triazole (TsPEAT, **16**) and 4-amino-3,5-bis({[2-(2-pyridyl)ethyl]amino}methyl)-4*H*-1,2,4-triazole (PEAT, **17**).

Encouraged by these results we examined the coupling of hydrochloride **8** and sulfonamide **11** (Scheme 4). This was expected to lead to the formation of 4-amino-3,5-bis({*N*-[2-(2-pyridyl)ethyl]-*N*-(4-toluenesulfonyl)amino}methyl)-4*H*-1,2,4-triazole (TsPEAT, **16**), which could then be converted into 4-amino-3,5-bis({[2-(2-pyridyl)ethyl]amino}methyl)-4*H*-1,2,4-triazole (PEAT, **17**). However, TsPEAT (**16**) could not be isolated from these experiments and only unchanged sulfonamide **11** was recovered, almost quantitatively, when the reaction was carried out under identical conditions as for TsPMAT (**14**). In fact, no 1,2,4-triazole compound of any kind was present in the filtered reaction mixture, as evidenced by ^{13}C NMR analysis of the residue after evaporation. Under the basic reaction conditions employed, the actual reactive species is dichloride **9**, formed in situ by the neutralisation of hydrochloride **8**. Considering the established instability of dichloride **9**, it presumably decomposed faster than it could react with sulfonamide **11**. This suggests a significant difference in reactivity between the two sulfonamides **10** and **11**. The polymeric material resulting from the decomposition of dichloride **9** was presumably filtered off along with the inorganic salts during workup. In summary, we could prepare the acyclic ligands TsPMAT (**14**) and PMAT (**15**) by this route, but their homologues TsPEAT (**16**) and PEAT (**17**) could not be prepared this way.

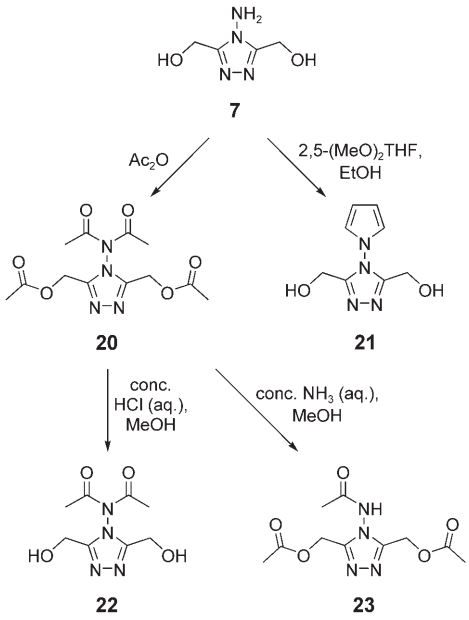
Aiming at macrocyclic ligand preparation, we initially attempted to couple hydrochloride **8** with sulfonamide **13**, again in *N*,*N*-dimethylformamide in the presence of potassium carbonate at 60 °C for 24 h. NMR and TLC analysis of the residue obtained after filtration of the reaction mixture and evaporation of the filtrate in vacuo showed that a mixture of several different compounds was present, including unreacted sulfonamide **13**, and indicated that some coupling had indeed occurred. However, prolonged reaction times did not result in the formation of a single species or the consumption of the remaining sulfonamide **13**, and isolation and identification of the reaction products proved to be very difficult. Given the problems faced earlier in the attempted synthesis of TsPEAT (**16**), further experiments to optimise the coupling of hydrochloride **8** with sulfonamide **13** were not carried out. Rather, the reactivity of the latter compound towards other, potentially more suitable, 1,2,4-triazole derivatives is currently being investigated.[19]

To overcome the problems caused by the presence of both the nucleophilic 4-amino group and the chloride leaving groups in hydrochloride **8** and dichloride **9**, a way was sought to eliminate the 4-amino group by derivatisation. Therefore, we prepared the two hitherto unknown compounds 4-(diacetylamino)-3,5-bis(chloromethyl)-4*H*-1,2,4-triazole (**18**) and 3,5-bis(chloromethyl)-4-(1*H*-pyrrol-1-yl)-4*H*-

1,2,4-triazole (**19**) as colourless crystalline solids in good yields, by the reaction of hydrochloride **8** with acetic anhydride or 2,5-dimethoxytetrahydrofuran,[66,67] respectively (Scheme 5). Dichlorides **18** and **19** were found to exhibit good thermal stability and to be readily soluble in organic



Scheme 5. Synthesis of 4-(diacetylamino)-3,5-bis(chloromethyl)-4*H*-1,2,4-triazole (**18**) and 3,5-bis(chloromethyl)-4-(1*H*-pyrrol-1-yl)-4*H*-1,2,4-triazole (**19**).



Scheme 6. Synthesis of 4-(diacetylamino)-4*H*-1,2,4-triazole-3,5-dimethyl diacetate (**20**) and 4-(1*H*-pyrrol-1-yl)-4*H*-1,2,4-triazole-3,5-dimethanol (**21**) and hydrolysis of the latter.

solvents. Initial attempts to couple dichlorides **18** and **19** with two simple nucleophiles, the sodium salts of 2-aminophenol and 4-toluenesulfonamide, indicate that dichloride **19** is the more promising candidate.[68] Coupling reactions of dichloride **19** with sulfonamides **10**, **11** and **13** are now being investigated and the results of these studies will be reported in due course.[19]

It should be noted that throughout these synthetic developments the possibility of developing access to new dicarbonyl head units that are more suitable than compounds **2**–**6** for the generation of Schiff base ligands has been borne in mind. Hence a brief, unsuccessful attempt was made to oxidise the highly polar dialcohol **7**, which is only soluble in water, dimethyl sulfoxide and *N*,*N*-dimethylformamide, to the corresponding dialdehyde. Given the increase in solubility noted when the 4-amino group in dichloride **8** was converted into either a 4-(diacetylamino) (**18**) or a 4-(1*H*-pyrrol-1-yl) (**19**) group, a similar approach was tried with dialcohol **7**, rather than pursuing its oxidation further. Specifically, derivatisation of dialcohol **7** generated 4-(diacetylamino)-4*H*-1,2,4-triazole-3,5-dimethyl diacetate (**20**) and 4-(1*H*-pyrrol-1-yl)-4*H*-1,2,4-triazole-3,5-dimethanol (**21**) (Scheme 6).

The acetylation of dialcohol **7** was carried out in essentially the same way as described by Adámek (Scheme 6).[51] Thus, a suspension of dialcohol **7** in an excess of acetic anhydride was refluxed for 30 min. Evaporation of all volatiles afforded a yellow oil that crystallised on drying in vacuo and was identified by ^{1}H and ^{13}C NMR spectroscopy as the tetraacetylated compound **20**. Recrystallisation of the crude product from ethanol gave pure tetraacetate **20** as colourless flakes in 62% yield. It is interesting to note that diacetylation of the 4-amino group of dialcohol **7** occurred, resulting in the formation tetraacetate **20**. This contradicted the findings of Adámek,[51] who had reported obtaining 4-amino-3,5-dimethyl-4*H*-1,2,4-triazole diacetate, that is, the diacetylated compound with the 4-amino group unchanged. It also contradicted the report of Voříšek,[69] who observed the formation of a triacetate, that is, monoacetylation of the 4-amino group, on acetylation of a related dialcohol. However, it was consistent with the observed diacetylation of 4-amino groups in related 1,2,4-triazoles reported by other research groups.[70,71] To obtain pure tetraacetate **20** in good yield it was crucial to reflux the reaction mixture vigorously and to immerse the reaction vessel in a preheated oil bath (160 °C) rather than increasing the temperature gradually. Inseparable mixtures of differently acetylated compounds were obtained when these directions were not followed. NMR data obtained on the crude products of preliminary experiments clearly indicate that stirring tetraacetate **20** with concentrated aqueous ammonia in methanol at room temperature for one hour facilitates the selective hydrolysis of this compound to triacetate **23**, which is readily soluble in chloroform and other organic solvents, whereas the use of concentrated hydrochloric acid in methanol appears to result in the formation of dialcohol **22**, the latter compound being insoluble in chloroform but readily soluble in dimethyl sulfoxide (Scheme 6).[68] Dialcohol **22** did not exhibit improved solubility in organic solvents over that of the original dialcohol(**7**), so to date its preparation has not been optimised.

We turned our attention to the reaction of dialcohol **7** with 2,5-dimethoxytetrahydrofuran in acetic acid[66,67] which gave pure dialcohol **21** as a greyish powder in 24% yield (Scheme 6). The synthesis of dialcohol **21** is currently being optimised, as it is proving to be a good starting material for further reactions.[19] To summarise, the preparation of more

convenient dialdehyde head units from such dialcohols (for example, **7**, **21** or **22**) is looking promising and is an active line of enquiry in this research group.[19] We are concurrently working on alternative strategies to access new 1,2,4-triazole-based head and lateral units.[19,68]

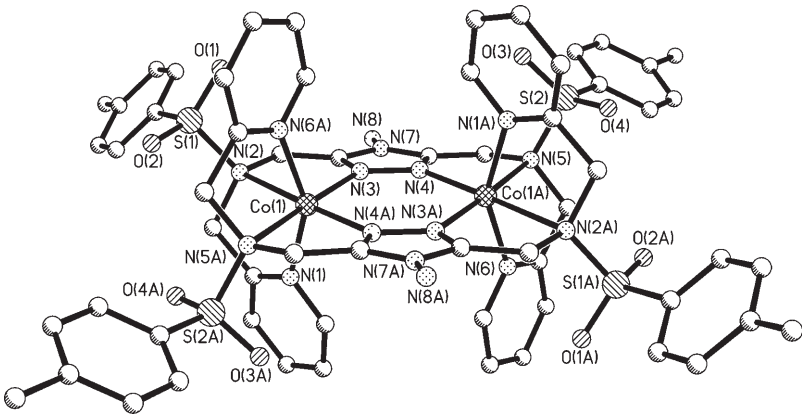


Figure 1. View of the molecular structure of the cation of $[Co^{II}_2(TsPMAT)_2](BF_4)_4 \cdot 6MeCN$ (**24**·6MeCN). Hydrogen atoms have been omitted for clarity. Selected distances [Å]: Co(1)–N(1) 2.048(5), Co(1)–N(2) 2.626(5), Co(1)–N(3) 2.062(5), Co(1)–N(4A) 2.028(5), Co(1)–N(5A) 2.551(5), Co(1)–N(6A) 2.044(5), Co(1)···Co(1A) 4.056(2). Selected angles [°]: N(1)-Co(1)-N(2) 73.3(2), N(1)-Co(1)-N(3) 91.6(2), N(1)-Co(1)-N(4A) 103.8(2), N(1)-Co(1)-N(5A) 94.2(2), N(1)-Co(1)-N(6A) 152.0(2), N(2)-Co(1)-N(3) 73.7(2), N(2)-Co(1)-N(4A) 171.6(2), N(2)-Co(1)-N(5A) 113.8(2), N(2)-Co(1)-N(6A) 88.9(2), N(3)-Co(1)-N(4A) 98.8(2), N(3)-Co(1)-N(5A) 171.6(2), N(3)-Co(1)-N(6A) 104.2(2), N(4A)-Co(1)-N(5A) 74.0(2), N(4A)-Co(1)-N(6A) 96.6(2), N(5A)-Co(1)-N(6A) 73.0(2), Co(1)-N(3)-N(4) 130.0(4), Co(1)-N(4A)-N(3A) 131.2(4). Symmetry operation used to generate equivalent atoms: (A) $-x+2$, $-y+2$, $-z+2$.

Complexes of TsPMAT: We expected TsPMAT (**14**) to be capable of acting as a dinucleating ligand offering two terdentate binding sites. While there are numerous examples in the literature of secondary sulfonamides coordinating to metal ions in their deprotonated form, there are, to the best of our knowledge, only two examples in which tertiary sulfonamides, notoriously weak donor groups, are bound to metal ions.[72,73] In the case of TsPMAT (**14**) the likelihood of the tertiary sulfonamides coordinating to the metal centres is improved due to the fact that these donors are well positioned within the two chelating N_3 binding pockets of the ligand.

The reaction of TsPMAT (**14**) with $Co(BF_4)_2 \cdot 6H_2O$ in both a 1:1 and a 1:2 ratio in refluxing ethanol gave a purple powder that was formulated as $[Co^{II}_2(TsPMAT)_2](BF_4)_4 \cdot 4H_2O$ (**24**·4H_2O) on the basis of its elemental analysis. The same compound was obtained when the reaction was carried out in either dry acetonitrile or laboratory reagent-grade acetonitrile to which a little water had been deliberately added, followed in both cases by precipitation with diethyl ether. The molar conductivity of complex **24**·4H_2O in acetonitrile was 441 $\Omega^{-1}cm^2mol^{-1}$, in good agreement with the expected value of 420–500 $\Omega^{-1}cm^2mol^{-1}$ for a 4:1 electrolyte.[74] Recrystallisation of complex **24**·4H_2O from acetonitrile by vapour diffusion of diethyl ether produced single crystals of $[Co^{II}_2(TsPMAT)_2](BF_4)_4 \cdot 6MeCN$ (**24**·6MeCN) suitable for an X-ray crystal structure analysis (Figure 1). This confirmed that TsPMAT (**14**) is indeed able to bind and bridge two metal ions. All twelve of the donor atoms to the two cobalt(II) centres are provided by the two ligand molecules, which fully encapsulate them, giving rise to a sandwich-like structure. The asymmetric unit comprises one half of the complex with the other half generated by a centre of inversion. The N_6 coordination sphere about the cobalt(II) centres is strongly distorted from octahedral with very much longer $Co–N_{sulfonamide}$ bonds (2.551(5) and 2.626(5) Å) than $Co–N_{pyridine}$ (2.044(5) and 2.048(5) Å) and $Co–N_{triazole}$ bonds (2.028(5) and 2.062(5) Å). The angles between *trans*-positioned donor atoms are considerably less than 180° with the N(1)-Co(1)-N(6A) angle between the axial pyridine nitrogen atoms showing the largest deviation from linearity (152.0(2)°). The mean planes of the two independent pyridine rings intersect with the CoN_4 mean plane, made up of the metal centre and the four equatorial nitrogen donors, at angles of 82.0(2) and 89.9(2)°, respectively. The Co···Co separation (4.056(2) Å) in this dinuclear cobalt(II) complex of the bis(terdentate) ligand TsPMAT (**14**) is significantly less than the corresponding distances (4.1481(7)–4.273(2) Å) observed in the handful of known dinuclear cobalt(II) complexes of bis(bidentate) 4-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles.[30,68,75,76] It is also significantly less than the Fe···Fe separations (4.2124(14) Å at 123 K and 4.297(2) Å at 298 K) observed in the dinuclear iron(II) complex of the very closely related bis(terdentate) ligand PMAT (**15**), $[Fe^{II}_2(PMAT)_2](BF_4)_4$·DMF (**27**·DMF) (see below), both at 123 K, when it contains one high-spin and one low-spin iron(II) centre, and at 298 K, when both iron(II) centres are high-spin.[31]

Measurements of magnetic properties carried out on a powder sample of complex **24**·4H_2O revealed that the two 1,2,4-triazole bridges mediate weak antiferromagnetic coupling between the two cobalt(II) centres, which are d^7 high-spin (Figure 2). The curve for the temperature dependence of the molar magnetic susceptibility showed a maximum at 19 K ($\chi_m = 0.05305\ cm^3mol^{-1}$), a feature characteristic of antiferromagnetic exchange coupling. The corresponding effective magnetic moment per cobalt(II) centre was found to be 4.30 μ_B at room temperature and gradually decreasing until a sharp drop occurred below approximately 50 K. The data were best fitted to an $S = 3/2$ dimer model using the parameters $J = -3.3\ cm^{-1}$ and $g = 2.26$. While cobalt(II) centres formally have $^4T_{1g}$ orbitally degenerate states, the low symme-

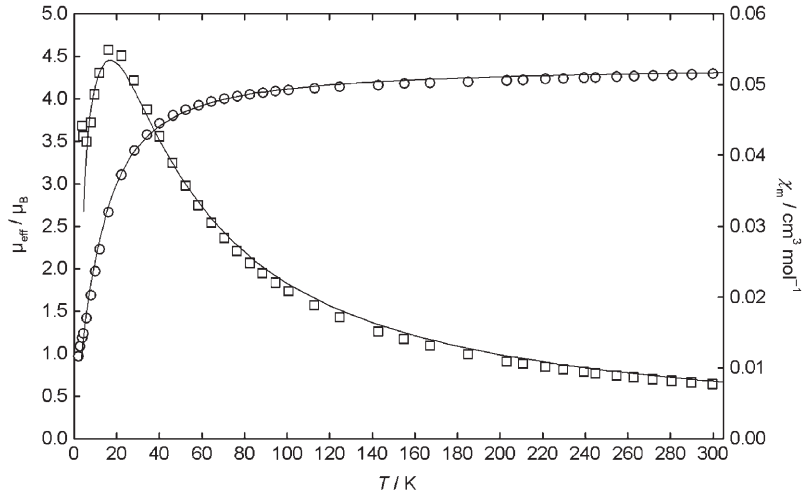


Figure 2. Temperature dependence of the effective magnetic moment μ_{eff} (○) and the molar magnetic susceptibility χ_m (□) for $[Co^{II}_2(TsPMAT)_2](BF_4)_4{\cdot}4H_2O$ (**24**·4 H_2O). The solid lines represent the best fit to an $S=3/2$ dimer model (see text).

try observed in the structure leads to orbital singlet behaviour, thus making a simple Heisenberg spin coupling model ($-2J\mathbf{S_1}{\cdot}\mathbf{S_2}$) a good approximation. The g value allows for spin-orbit coupling effects. The small value of J is similar in magnitude and sign to those of other 1,2,4-triazole-bridged dinuclear cobalt(II) systems[15,26,30,77] and a little lower, on average, than in related pyridazine-bridged species.[9,14,16]

The reactivity of TsPMAT (**14**) was also tested towards a few other d-block ions, but with very limited success. By using $Ni(BF_4)_2{\cdot}6H_2O$ a green crystalline but heterogeneous material was obtained, the identity of which could not be readily established. In the case of $Cu(BF_4)_2{\cdot}4H_2O$ a dark-green oily material was formed. A more defined product could only be isolated from the reaction of $Fe(BF_4)_2{\cdot}6H_2O$ with TsPMAT (**14**), by using the same reaction conditions as for the preparation of the cobalt(II) complex **24**·4 H_2O. This was tentatively formulated as $[Fe^{II}_2(TsPMAT)_2](BF_4)_4$ (**25**) on the basis of its elemental analysis. Complex **25** was obtained as an almost colourless solid that quickly turned yellow-brown when taken out of the mother liquor or handled in air. Even when it was prepared under a protective nitrogen atmosphere, it could only be isolated in impure form which prevented its proper characterisation. It is interesting to note that, in contrast, the cobalt(II) analogue **24**·4 H_2O did not exhibit such pronounced air-sensitivity. Even in acetonitrile the latter complex was oxidised only very slowly when exposed to air and was reasonably stable for a few days, as evidenced by the fact that it could be recrystallised successfully in air. Given the very interesting magnetic properties of $[Fe^{II}_2(PMAT)_2](BF_4)_4$·DMF (**27**·DMF) (see below), complex **25**, while air-sensitive, is the topic of further work.[19]

Complexes of PMAT: Similarly to TsPMAT (**14**), the amine congener PMAT (**15**) did not give complexes with a metal-to-ligand molar ratio of 2:1 when it was treated with hydrated first-row transition-metal tetrafluoroborates or perchlorates and dinuclear 2:2 complexes were obtained instead. All subsequent reactions were therefore carried out by using a metal-to-ligand molar ratio of 1:1. Thus, the reaction of PMAT (**15**) with $Mn(ClO_4)_2{\cdot}6H_2O$ or $M(BF_4)_2{\cdot}6H_2O$ (M = Fe, Co, Ni, Zn) in acetonitrile readily gave the five corresponding complexes with the general formula $[M^{II}_2(PMAT)_2]X_4$ as powdery solids. All members of this series, except $[Ni^{II}_2(PMAT)_2](BF_4)_4$ (**29**), which was obtained in only 28% yield, were practically insoluble in acetonitrile and precipitated straight from the reaction mixture in yields greater than 70%. The yield of the more soluble nickel(II) complex, **29**, was improved by the addition of diethyl ether to the initial filtrate as crystals were grown from the filtrate this way (see below). The molar conductivities (230–265 $\Omega^{-1}cm^2mol^{-1}$) of all five complexes, **26**–**30**, were at the low-end of the expected range for 4:1 electrolytes in *N*,*N*-dimethylformamide (240–300 $\Omega^{-1}cm^2mol^{-1}$).[74] The iron(II) complex **27** and the cobalt(II) complex **28** did not seem to be sensitive towards oxygen in the solid state. However, solutions of the cobalt(II) complex **28** in *N*,*N*-dimethylformamide turned dark-brown within a few hours when left to stand in air, presumably due to oxidation of the metal centres. The solubility of the zinc(II) complex **30** was too low, even in deuterated *N*,*N*-dimethylformamide, to obtain a ^{13}C NMR spectrum showing all expected peaks, even when the experiment was run for an extended period of time. The ^1H NMR spectrum of this complex in deuterated *N*,*N*-dimethylformamide was inconclusive and broad split peaks were observed that could not be assigned.

The X-ray crystal structures of the half-spin-crossover form LS–HS (at 123 K) and of the complete high-spin form HS–HS (at 298 K) of $[Fe^{II}_2(PMAT)_2](BF_4)_4$·DMF (**27**·DMF) have been described in a preliminary communication.[31] The two bis(terdentate) molecules of PMAT (**15**) sandwich the two iron(II) centres resulting in an overall architecture analogous to that of the dinuclear cobalt(II) complex of TsPMAT (**14**), $[Co^{II}_2(TsPMAT)_2](BF_4)_4{\cdot}6MeCN$ (**24**·6 MeCN) (Figure 1). Crystals of complex **27**·DMF were obtained by slow evaporation of a solution of complex **27** in acetonitrile/*N*,*N*-dimethylformamide. We attempted various methods to crystallise the nickel(II) complex **29**, the most soluble member of this series. Vapour diffusion of diethyl ether into a solution of the initially obtained powder in acetonitrile failed to produce single crystals, whereas application of the same technique to the acetonitrile mother liquor

occasionally afforded a crystalline material. Unfortunately, the X-ray data collected on this material were of insufficient quality. Attempts to recrystallise the other complexes, **26**, **28** and **30**, using these and other methods failed. It is expected that all of these complexes have the same overall sandwich-like architecture as that observed in complexes **24**·6 MeCN and **27**·DMF, although it should be noted that, in principle, each of the two molecules of PMAT (**15**) may bind with the two pyridine rings coordinating to the two metal centres from the same side (as seen in Figure 1) or from opposite sides, that is, one from above and the other from underneath.

In addition to the magnetic studies carried out to date on the iron(II) complex **27**·DMF,[31] we examined the magnetic properties of $[Mn^{II}_2(PMAT)_2](ClO_4)_4$ (**26**) and $[Co^{II}_2(PMAT)_2](BF_4)_4$ (**28**). Weak antiferromagnetic coupling between the two metal centres was observed in both complexes. The room-temperature effective magnetic moment per manganese centre for the manganese(II) complex **26** was 5.98 μ_B (Figure S1 in the Supporting Information) and thus in very good agreement with the expected value of 5.92 μ_B for a spin-only d^5 high-spin system. The corresponding value for complex **28** was 4.42 μ_B (Figure S2 in the Supporting Information), revealing that the cobalt(II) centres were d^7 high-spin by analogy to the related cobalt(II) complex **24**·4 H_2O of TsPMAT (**14**). The curve for the molar magnetic susceptibility of the cobalt(II) complex **28** reached a maximum at $T = 11$ K with $\chi_m = 0.0825\ cm^3\,mol^{-1}$, while for the manganese(II) complex **26** no maximum was observed in the accessible temperature range of 300–4.2 K. The data were best fitted to an $S = 5/2$ dimer model for the manganese(II) complex **26** and an $S = 3/2$ dimer model for the cobalt(II) complex **28** using the parameters $J = -0.16\ cm^{-1}$, $g = 2.02$ and 1% monomer, and $J = -2.4\ cm^{-1}$, $g = 2.31$ and $TIP = 90 \times 10^{-6}\ cm^3\,mol^{-1}$, respectively.

Conclusion

We have been able to synthesise the two novel ligands TsPMAT (**14**) and PMAT (**15**) which are hydrolytically stable and isolable as the metal-free compounds by using an approach based on nucleophilic substitution rather than Schiff base condensation. To the best of our knowledge, to date these ligands are the only examples of bis(terdentate) ligands capable of bridging two metal ions by means of a central 1,2,4-triazole moiety. It was expected that these bis(terdentate) ligands would facilitate the formation of dinuclear doubly 1,2,4-triazole-bridged complexes, $[M_2L_2]^{2n+}$, over mononuclear complexes, $[ML_2]^{n+}$, to a much greater extent than is observed with related bis(bidentate) 1,2,4-triazole-based ligands.[21,30,76] This has been borne out by experiment with the formation of a series of $[M_2L_2]^{2n+}$ complexes, **24**–**30**. While the methodology employed for the synthesis of these two bis(terdentate) ligands, TsPMAT (**14**) and PMAT (**15**), could not be extended to the analogous systems TsPEAT (**16**) and PEAT (**17**), presumably due to the instability of the 1,2,4-triazole component used in these experiments, the usefulness of this approach has clearly been demonstrated. We anticipate that the use of the hitherto unknown dichlorides **18** and **19**, which do not have a free 4-amino group on the 1,2,4-triazole ring, will facilitate the synthesis of analogous ligand systems, the complexes of which might well exhibit better crystallisation behaviour. Work in this direction is in progress and the results will be reported in due course.[19]

Experimental Section

General remarks: Melting points were determined with a Gallenkamp melting point apparatus in open-glass capillary tubes and are uncorrected. Elemental analyses were carried out by the Campbell Microanalytical Laboratory at the University of Otago. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-300 (or INOVA-500) spectrometer at 25 °C. For spectra recorded in deuterated chloroform ($\delta_H = 7.26$ ppm; $\delta_C = 77.16$ ppm) or deuterated dimethyl sulfoxide ($\delta_H = 2.50$ ppm; $\delta_C = 39.52$ ppm) chemical shifts are quoted relative to tetramethylsilane (TMS) with the residual solvent signal as secondary reference.[78] IR spectra were obtained on a Perkin–Elmer Spectrum BX FTIR spectrophotometer. ESI mass spectra were run on a Shimadzu LCMS-QP8000α spectrometer in acetonitrile. Molar conductivities were measured with a Suntex SC-170 conductivity meter at 25 °C. Magnetic data were recorded over the range 300–4.2 K using a Quantum Design MPMS5 SQUID magnetometer with an applied field of 1 T. Commercially available materials were used as received. *N*-(3-Aminopropyl)acetamide (**12**) was prepared as previously described.[65]

Caution: While no problems were encountered in the course of this work, reactions involving hydrazine hydrate may form potentially explosive mixtures so must be carried out with extreme caution. Similarly, ClO_4^- salts are potentially explosive so should be handled with appropriate care.

4-Amino-4*H*-1,2,4-triazole-3,5-dimethanol (7): Hydrazine monohydrate (37.5 g, 0.75 mol) was added dropwise at 0 °C to 70% aqueous glycolic acid (54.3 g, 0.50 mol). The resulting solution was heated at 120 °C for 6 h. Then the reflux condenser was replaced with a downward condenser and the reaction mixture was heated at 160 °C for a further 18 h allowing excess hydrazine and water to distil off. After cooling, the resulting yellowish crystalline solid was recrystallised from water to give analytically pure **7** (21.1 g, 58%) as colourless flakes. M.p. 206–208 °C; elemental analysis calcd (%) for $C_4H_8N_4O_2$ (144.13): C 33.33, H 5.59, N 38.87; found: C 33.29, H 5.41, N 39.05; ^1H NMR (300 MHz, [D$_6$]DMSO): $\delta =$ 4.54 (d, $^3J = 6.0$ Hz, 4H; 2×TzCH_2OH), 5.37 (t, $^3J = 6.0$ Hz, 2H; 2×TzCH$_2$O*H*), 5.81 ppm (s, 2H; TzNH_2); $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]DMSO): $\delta = 52.7$ (2×TzCH$_2$OH), 154.4 ppm (3-, 5-Tz*C*); IR (KBr): $\tilde{\nu} =$ 3344, 3220, 2877, 2687, 1639, 1518, 1479, 1461, 1440, 1379, 1351, 1305, 1280, 1204, 1068, 1029, 976, 953, 875, 819, 774, 720, 498 cm^{-1}.

4-Amino-3,5-bis(chloromethyl)-4*H*-1,2,4-triazole monohydrochloride (8): A suspension of compound **7** (28.8 g, 0.20 mol) in thionyl chloride (80 mL) was stirred at room temperature for 8 h, during which time a vigorous exothermic reaction took place. Excess thionyl chloride was removed under reduced pressure and the resulting yellowish solid was dried in vacuo. Recrystallisation from ethanol gave analytically pure **8** (33.4 g; 76%) as colourless needles. M.p. 139–141 °C; elemental analysis calcd (%) for $C_4H_7Cl_3N_4$ (217.48): C 22.09, H 3.24, N 25.76; found: C 22.24, H 3.24, N 25.83; ^1H NMR (300 MHz, [D$_6$]DMSO): $\delta = 4.92$ ppm (s, 4H; 2×TzCH_2Cl); $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]DMSO): $\delta = 32.9$ (2×TzCH_2Cl), 152.5 ppm (3-, 5-Tz*C*); IR (KBr): $\tilde{\nu} =$ 3414, 3253, 3145, 2970, 2642, 1637, 1617, 1576, 1417, 1328, 1264, 1165, 1105, 1034, 975, 937, 919, 888, 807, 759, 668, 646, 605, 568, 513 cm^{-1}.

4-Amino-3,5-bis(chloromethyl)-4*H*-1,2,4-triazole (9): Sodium hydrogen carbonate (3.36 g, 40.0 mmol) was added in portions to a vigorously stir-

red heterogeneous mixture of compound **8** (8.70 g, 40.0 mmol), water (50 mL) and ethyl acetate (50 mL). After complete addition, the layers were separated and the aqueous layer was extracted with ethyl acetate (3×25 mL). The combined organic layers were dried over anhydrous sodium sulfate. Evaporation of the solvent under reduced pressure gave analytically pure **9** (6.34 g, 87%) as a colourless crystalline solid. M.p. 97–99°C; elemental analysis calcd (%) for $C_4H_6Cl_2N_4$ (181.02): C 26.54, H 3.34, N 30.95; found: C 26.88, H 3.33, N 30.98; ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ=4.87 (s, 4H; 2×TzCH_2Cl), 6.12 ppm (s, 2H; TzNH_2); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]DMSO): δ=33.0 (2×TzCH_2Cl), 152.2 ppm (3-, 5-TzC); IR (KBr): $\tilde{\nu}$=3414, 3233, 3115, 1659, 1637, 1616, 1514, 1482, 1423, 1370, 1286, 1261, 1246, 1162, 1144, 1079, 984, 921, 800, 758, 730, 683, 607, 490 cm^{-1}.

***N*-(2-Pyridylmethyl)-4-toluenesulfonamide hemihydrate (10·0.5 H$_2$O)**: A solution of 4-toluenesulfonyl chloride (7.63 g, 40.0 mmol) in tetrahydrofuran (40 mL) was added dropwise at room temperature to a solution of 2-(aminomethyl)pyridine (4.33 g, 40.0 mmol) and sodium hydroxide (1.60 g, 40.0 mmol) in water (40 mL). The resulting heterogeneous mixture was stirred vigorously at room temperature for 2 h. Then the tetrahydrofuran was evaporated under reduced pressure to crystallise the product from the remaining aqueous phase. It was filtered off, washed with water, and dried in air. Recrystallisation from ethanol gave analytically pure **10**·0.5 H$_2$O (8.38 g, 77%) as colourless rods. M.p. 95–97°C; elemental analysis calcd (%) for $C_{13}H_{15}N_2O_{2.5}S$ (271.34): C 57.54, H 5.57, N 10.32, S 11.82; found: C 57.47, H 5.71, N 10.39, S 11.83; ^{1}H NMR (300 MHz, CDCl$_3$): δ=2.39 (s, 3H; PhCH_3), 4.24 (d, ^3J=5.4 Hz, 2H; SO_2NHCH_2), 6.10 (t, ^3J=5.4 Hz, 1H; SO_2NHCH_2), 7.15 (ddd, $^3J_{4,5}$=7.7 Hz, $^3J_{5,6}$=4.8 Hz, $^4J_{3,5}$=1.2 Hz, 1H; 5-Py*H*), 7.18 (ddd, $^3J_{3,4}$=7.7 Hz, $^4J_{3,5}$=1.2 Hz, $^5J_{3,6}$=0.9 Hz, 1H; 3-Py*H*), 7.24 (d, ^3J=8.4 Hz, 2H; 3-, 5-Ph*H*), 7.60 (dt, $^3J_{3,4}$=$^3J_{4,5}$=7.7 Hz, $^4J_{4,6}$=1.8 Hz, 1H; 4-Py*H*), 7.73 (d, ^3J=8.4 Hz, 2H; 2-, 6-Ph*H*), 8.44 ppm (ddd, $^3J_{5,6}$=4.8 Hz, $^4J_{4,6}$=1.8 Hz, $^5J_{3,6}$=0.9 Hz, 1H; 6-Py*H*); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ=21.5 (PhCH_3), 47.5 (SO_2NHCH_2), 122.0 (3-Py*C*), 122.6 (5-Py*C*), 127.2 (2-, 6-Ph*C*), 129.6 (3-, 5-Ph*C*), 136.7 (1-Ph*C*), 136.8 (4-Py*C*), 143.3 (4-Ph*C*), 149.0 (6-Py*C*), 155.0 ppm (2-Py*C*); IR (KBr): $\tilde{\nu}$=3414, 3093, 2879, 1928, 1667, 1638, 1616, 1599, 1574, 1492, 1466, 1442, 1430, 1385, 1329, 1308, 1287, 1240, 1165, 1111, 1090, 1053, 1007, 852, 819, 763, 662, 605, 553, 544 cm^{-1}. Drying of compound **10**·0.5 H$_2$O in vacuo at 60°C for three days gave analytically pure **10** as dull colourless crystals. Elemental analysis calcd (%) for $C_{13}H_{14}N_2O_2S$ (262.33): C 59.52, H 5.38, N 10.68, S 12.22; found: C 59.44, H 5.39, N 10.55, S 12.27.

***N*-[2-(2-Pyridyl)ethyl]-4-toluenesulfonamide (11)**: The procedure described above for the preparation of compound **10** was followed using 2-(2-aminoethyl)pyridine (4.89 g, 40.0 mmol), 4-toluenesulfonyl chloride (7.63 g, 40.0 mmol) and sodium hydroxide (1.60 g, 40.0 mmol) in water (40 mL) and tetrahydrofuran (40 mL) to obtain analytically pure **11** (9.11 g, 82%) as colourless blocks after recrystallisation from ethanol. M.p. 118–120°C; elemental analysis calcd (%) for $C_{14}H_{16}N_2O_2S$ (276.36): C 60.85, H 5.84, N 10.14, S 11.60; found: C 60.70, H 5.91, N 10.16, S 11.64; ^{1}H NMR (300 MHz, CDCl$_3$): δ=2.40 (s, 3H; PhCH_3), 2.93 (t, ^3J=6.0 Hz, 2H; PyCH_2), 3.34 (q, ^3J=6.0 Hz, 2H; SO_2NHCH_2), 6.25 (t, ^3J=6.0 Hz, 1H; SO_2NHCH_2), 7.07 (ddd, $^3J_{3,4}$=7.7 Hz, $^4J_{3,5}$=1.2 Hz, $^5J_{3,6}$=0.9 Hz, 1H; 3-Py*H*), 7.12 (ddd, $^3J_{4,5}$=7.7 Hz, $^3J_{5,6}$=4.8 Hz, $^4J_{3,5}$=1.2 Hz, 1H; 5-Py*H*), 7.26 (d, $^3J_{2,3}$=8.4 Hz, 2H; 3-, 5-Ph*H*), 7.57 (dt, $^3J_{3,4}$=$^3J_{4,5}$=7.7 Hz, $^4J_{4,6}$=1.8 Hz, 1H; 4-Py*H*), 7.72 (d, $^3J_{2,3}$=8.4 Hz, 2H; 2-, 6-Ph*H*), 8.45 ppm (ddd, $^3J_{5,6}$=4.8 Hz, $^4J_{4,6}$=1.8 Hz, $^5J_{3,6}$=0.9 Hz, 1H; 6-Py*H*); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ=21.5 (PhCH_3), 36.3 (PyCH_2), 42.3 (SO_2NHCH_2), 121.7 (5-Py*C*), 123.5 (3-Py*C*), 127.0 (2-, 6-Ph*C*), 129.6 (3-, 5-Ph*C*), 136.7 (4-Py*C*), 137.2 (1-Ph*C*), 143.1 (4-Ph*C*), 149.0 (6-Py*C*) 158.9 ppm (2-Py*C*); IR (KBr): $\tilde{\nu}$=3474, 3055, 2856, 1636, 1616, 1595, 1569, 1493, 1476, 1439, 1324, 1303, 1287, 1155, 1092, 916, 820, 763, 660, 631, 593, 561, 546, 502 cm^{-1}.

***N*-{3-[(4-Toluenesulfonyl)amino]propyl}acetamide (13)**: A solution of 4-toluenesulfonyl chloride (24.8 g, 0.13 mol) in tetrahydrofuran (100 mL) was added within 30 min to a solution of **12**[65] (15.1 g, 0.13 mol) and sodium hydrogen carbonate (10.9 g, 0.13 mol) in water (100 mL). The resulting heterogeneous mixture was then stirred vigorously at room temperature for 18 h. The resulting solution was evaporated under reduced pressure and the residue was taken up in chloroform (100 mL). The insoluble materials were filtered off and washed with chloroform. The filtrate was evaporated under reduced pressure to give a thick, yellowish oil. Trituration with ethyl acetate (100 mL) gave a colourless solid which was filtered off and washed with ethyl acetate. Drying in vacuo gave **13** (32.5 g, 92%) as a colourless fluffy powder. This material was used in subsequent reactions without further purification. An analytically pure sample was obtained as colourless blocks by recrystallisation from 1,4-dioxane. M.p. 100–102°C; elemental analysis calcd (%) for $C_{12}H_{18}N_2O_3S$ (270.35): C 53.31, H 6.71, N 10.36, S 11.86; found: C 53.42, H 6.40, N 10.26, S 12.01; ^{1}H NMR (300 MHz, CDCl$_3$): δ=1.64 (quint, ^3J=6.3 Hz, 2H; CH_2CH$_2$NHSO$_2$), 1.93 (s, 3H; CH_3CONHCH$_2$), 2.41 (s, 3H; PhCH_3), 2.91 (q, ^3J=6.3 Hz, 2H; CH$_2$CH_2NHSO$_2$), 3.30 (q, ^3J=6.3 Hz, 2H; CH$_3$CONHCH_2), 5.74 (t, ^3J=6.3 Hz, 1H; CH$_2$CH$_2$N*H*SO$_2$), 6.08 (t, ^3J=6.3 Hz, 1H; CH$_3$CON*H*CH$_2$), 7.29 (d, ^3J=8.2 Hz, 2H; 3-, 5-Ph*H*), 7.73 ppm (d, ^3J=8.2 Hz, 2H; 2-, 6-Ph*H*); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ=21.8 (PhCH_3), 23.4 (*C*H$_3$CONHCH$_2$), 29.9 (*C*H$_2$CH$_2$NHSO$_2$), 36.4 (CH$_3$CONH*C*H$_2$), 40.3 (CH$_2$*C*H$_2$NHSO$_2$), 127.3 (2-, 6-Ph*C*), 130.0 (3-, 5-Ph*C*), 137.4 (4-Ph*C*), 143.6 (1-Ph*C*), 171.5 ppm (CH$_3$*C*ONHCH$_2$); IR (KBr): $\tilde{\nu}$=3372, 3143, 2934, 2861, 1656, 1596, 1550, 1497, 1458, 1430, 1370, 1323, 1310, 1213, 1162, 1092, 1065, 967, 923, 868, 811, 777, 734, 661, 578, 551, 512, 475 cm^{-1}.

4-Amino-3,5-bis{[*N*-(2-pyridylmethyl)-*N*-(4-toluenesulfonyl)amino]methyl}-4*H*-1,2,4-triazole (TsPMAT, 14): A mixture of compound **8** (2.17 g, 10.0 mmol), **10**·0.5 H$_2$O (5.43 g, 20.0 mmol), and potassium carbonate (8.29 g, 60.0 mmol) in *N*,*N*-dimethylformamide (100 mL) was heated at 60°C for 24 h. After cooling, the suspension was filtered and the clear orange filtrate was evaporated under reduced pressure. The remaining oil was thoroughly dried in vacuo to give a brown paste which was redissolved in dichloromethane (50 mL). The cloudy solution was filtered through a short pad of celite. Evaporation of the solvent and drying in vacuo gave a brownish foam which was taken up in ethanol (50 mL). On standing at room temperature, the product separated from the solution. It was filtered off and washed with a minimum amount of ethanol. Drying in vacuo gave analytically pure **14** (3.81 g, 60%) as a colourless powder. Elemental analysis calcd (%) for $C_{30}H_{32}N_8O_4S_2$ (632.76): C 56.95, H 5.10, N 17.71, S 10.13; found: C 56.57, H 4.96, N 17.65, S 10.02; ^{1}H NMR (500 MHz, CDCl$_3$): δ=2.45 (s, 6H; 2×PhCH_3), 4.44 (s, 4H; 2×PyCH_2), 4.51 (s, 4H; 2×TzCH_2), 5.57 (s, 2H; TzNH_2), 7.11 (ddd, $^3J_{4,5}$=7.7 Hz, $^3J_{5,6}$=4.8 Hz, $^4J_{3,5}$=1.2 Hz, 2H; 2×5-Py*H*), 7.24 (ddd, $^3J_{3,4}$=7.7 Hz, $^4J_{3,5}$=1.2 Hz, $^5J_{3,6}$=0.9 Hz, 2H; 2×3-Py*H*), 7.31 (d, $^3J_{2,3}$=8.4 Hz, 4H; 2×3-, 5-Ph*H*), 7.57 (dt, $^3J_{3,4}$=$^3J_{4,5}$=7.7 Hz, $^4J_{4,6}$=1.8 Hz, 2H; 2×4-Py*H*), 7.73 (d, $^3J_{2,3}$=8.4 Hz, 4H; 2×2-, 6-Ph*H*), 8.41 ppm (ddd, $^3J_{5,6}$=4.8 Hz, $^4J_{4,6}$=1.8 Hz, $^5J_{3,6}$=0.9 Hz, 2H; 2×6-Py*H*); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ=21.8 (2×PhCH_3), 42.6 (2×TzCH_2), 53.2 (2×PyCH_2) 122.7 (2×3-Py*C*), 122.8 (2×5-Py*C*), 127.7 (2×2-, 6-Ph*C*), 130.0 (2×3-, 5-Ph*C*), 135.5 (2×1-Ph*C*), 137.0 (2×4-Py*C*), 144.1 (2×4-Ph*C*), 149.3 (2×6-Py*C*), 150.5 (3-, 5-Tz*C*), 156.2 ppm (2×2-Py*C*); IR (KBr): $\tilde{\nu}$=3424, 1636, 1617, 1591, 1569, 1520, 1493, 1476, 1436, 1342, 1305, 1162, 1101, 931, 908, 892, 814, 765, 660, 605, 556, 541 cm^{-1}; ESI-MS (positive mode, MeCN): *m*/*z*: 633 [*M*+H]$^+$.

4-Amino-3,5-bis{[(2-pyridylmethyl)amino]methyl}-4*H*-1,2,4-triazole (PMAT, 15): Compound **14** (1.27 g, 2.00 mmol) was dissolved in concentrated sulfuric acid (20 mL) and the reaction mixture was heated at 100°C for 8 h. After cooling, the almost colourless solution was basified by slow and careful addition of aqueous sodium hydroxide (60 mL, 15 M) at 0°C. Chloroform (50 mL) was added to the suspension and the solids were allowed to settle. The supernatant layers were decanted off and then separated. The aqueous layer was further extracted with chloroform (3×50 mL). The combined organic layers were dried over anhydrous sodium sulfate. Evaporation of the solvent gave **15** (0.64 g, 98%) as a colourless oil. This material was used in subsequent reactions without further purification. ^{1}H NMR (500 MHz, CDCl$_3$): δ=2.57 (s, 2H; 2×TzCH$_2$N*H*), 3.86 (s, 4H; 2×PyCH_2), 3.98 (s, 4H; 2×TzCH_2), 5.66 (s, 2H; TzNH_2), 7.13 (ddd, $^3J_{4,5}$=7.7 Hz, $^3J_{5,6}$=4.8 Hz, $^4J_{3,5}$=1.2 Hz, 2H; 2×5-Py*H*), 7.21 (ddd, $^3J_{3,4}$=7.7 Hz, $^4J_{3,5}$=1.2 Hz, $^5J_{3,6}$=0.9 Hz, 2H; 2×3-Py*H*), 7.60 (dt, $^3J_{3,4}$=$^3J_{4,5}$=7.7 Hz, $^4J_{4,6}$=1.8 Hz, 2H; 2×4-Py*H*), 8.49 ppm (ddd, $^3J_{5,6}$=4.8 Hz, $^4J_{4,6}$=1.8 Hz, $^5J_{3,6}$=0.9 Hz, 2H; 2×6-Py*H*); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ=42.9 (2×TzCH$_2$), 54.0 (2×PyCH$_2$), 122.3 (2×5-

Py*C*), 122.7 (2×3-Py*C*), 136.7 (2×4-PyC), 149.3 (2×6-Py*C*) 152.8 (3-, 5-Tz*C*) 158.8 ppm (2×2-PyC); ESI-MS (positive mode MeCN): $m/z = 325$ $[M+H]^+$.

4-(Diacetylamino)-3,5-bis(chloromethyl)-4*H*-1,2,4-triazole (18): A suspension of compound **8** (10.9 g, 50.0 mmol) in acetic anhydride (75 mL) was quickly heated to 140 °C and the resulting yellowish solution was kept at this temperature for another 10 min, during which time an orange solution was obtained. After cooling, all volatiles were removed in vacuo to give an orange crystalline solid which was recrystallised from ethanol to give analytically pure **18** (8.33 g, 62 %) as fine colourless needles. M.p. 150–152 °C; elemental analysis calcd (%) for $C_8H_{10}Cl_2N_4O_2$ (265.10): C 36.25, H 3.80, N 21.13; found: C 36.50, H 3.55, N 20.97; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.48$ (s, 6H; 2×CH_3CON), 4.60 ppm (s, 4H; 2×TzCH_2Cl); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 25.1$ (2×CH_3CON), 32.8 (2×TzCH_2Cl), 151.2 (3-, 5-Tz*C*), 169.4 ppm (2×CH_3*C*ON); IR (KBr): $\tilde{\nu} = 3455$, 3044, 3005, 2360, 2343, 1750, 1736, 1637, 1541, 1517, 1455, 1435, 1413, 1370, 1310, 1282, 1258, 1233, 1193, 1174, 1147, 1053, 1033, 1019, 941, 797, 751, 706, 665, 626, 592, 493 cm^{-1}.

3,5-Bis(chloromethyl)-4-(1*H*-pyrrol-1-yl)-4*H*-1,2,4-triazole (19): A mixture of compound **8** (21.8 g, 0.10 mol) and 2,5-dimethoxytetrahydrofuran (13.2 g, 0.10 mol) in ethanol (100 mL) was refluxed for 2 h, during which time a purplish-black solution was obtained. On cooling, the product crystallised out. It was filtered off, washed with ethanol and dried in vacuo to give analytically pure **19** (16.2 g, 70 %) as fine colourless needles. M.p. 142–144 °C; elemental analysis calcd (%) for $C_8H_8Cl_2N_4$ (231.09): C 41.58, H 3.49, N 24.25; found: C 41.87, H 3.56, N 24.21. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.50$ (s, 4H; 2×TzCH_2Cl), 6.41 (t, ^3J = 2.4 Hz, 2H; 3-, 4-Pl*H*), 6.89 ppm (t, $^3J = 2.4$ Hz, 2H; 2-, 5-Pl*H*); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 31.8$ (2×TzCH_2Cl), 110.5 (3-, 4-Pl*C*), 121.9 (2-, 5-Pl*C*), 152.0 ppm (3-, 5-Tz*C*). IR (KBr): $\tilde{\nu} = 3413$, 3131, 3118, 3028, 2973, 1512, 1454, 1423, 1344, 1335, 1267, 1168, 1148, 1122, 1064, 1027, 1005, 919, 842, 799, 751, 734, 705, 651, 584, 475, 454 cm^{-1}.

4-(Diacetylamino)-4*H*-1,2,4-triazole-3,5-dimethyl diacetate (20): A suspension of compound **7** (2.88 g, 20.0 mmol) in acetic anhydride (20 mL) was refluxed vigorously for 30 min, during which time a yellow solution was obtained. After cooling, all volatiles were removed in vacuo to give a yellow oil, which crystallised on standing. Recrystallisation from ethanol gave analytically pure **20** (3.90 g, 62 %) as colourless flakes. M.p. 109–111 °C; elemental analysis calcd (%) for $C_{12}H_{16}N_4O_6$ (312.28): C 46.15, H 5.16, N 17.94; found: C 46.21, H 5.22, N 18.23; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.06$ (s, 6H; 2×CH_3CON), 2.38 (s, 6H; 2×CH_3COO), 5.16 ppm (s, 4H; 2×TzCH_2); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 20.3$ (2×CH_3CON), 24.5 (2×CH_3COO), 54.7 (2×TzCH_2), 150.4 (3-, 5-Tz*C*), 169.3 (2×CH_3*C*OO), 169.5 ppm (2×CH_3*C*ON); IR (KBr): $\tilde{\nu} = 3477$, 1751, 1729, 1636, 1618, 1531, 1451, 1430, 1373, 1295, 1271, 1230, 1201, 1074, 1049, 1019, 944, 896, 836, 797, 756, 601 cm^{-1}.

4-(1*H*-Pyrrol-1-yl)-4*H*-1,2,4-triazole-3,5-dimethanol (21): A mixture of compound **7** (2.88 g, 20.0 mmol) and 2,5-dimethoxytetrahydrofuran (2.64 g, 20.0 mmol) in acetic acid (50 mL) was refluxed for 30 min to give an almost black solution. After cooling, all volatiles were removed in vacuo. The solid residue was suspended in ethanol (50 mL) and the mixture was refluxed for 30 min. After cooling, the remaining solid was filtered off and washed with ethanol. Drying in vacuo gave analytically pure **21** (0.94 g, 24 %) as a greyish powder. M.p. 202–204 °C; elemental analysis calcd (%) for $C_8H_{10}N_4O_2$ (194.19): C 49.48, H 5.19, N 28.85; found: C 49.39, H 5.31, N 28.80; IR (KBr): $\tilde{\nu} = 3210$, 3143, 2854, 1524, 1456, 1436, 1395, 1355, 1333, 1218, 1124, 1065, 1026, 978, 949, 913, 812, 724, 680, 580, 499, 466, 420 cm^{-1}.

$[Co^{II}_2(TsPMAT)_2](BF_4)_4$·4$H_2O$ (24·4H_2O): A pink solution of $Co(BF_4)_2$·6H_2O (68 mg, 0.20 mmol) in ethanol (10 mL) was added dropwise to a refluxing colourless solution of compound **14** (127 mg, 0.20 mmol) in ethanol (20 mL). The resulting clear purple solution was refluxed for a further 30 min, during which time the product precipitated from the reaction mixture. After cooling, the solid was filtered off and washed with ethanol and diethyl ether. Drying in vacuo gave **24**·4H_2O (139 mg, 77 %) as a pale purple powder. Elemental analysis calcd (%) for $C_{60}H_{72}B_4Co_2F_{16}N_{16}O_{12}S_4$ (1802.68): C 39.98, H 4.03, N 12.43, S 7.12; found: C 40.36, H 3.89, N 12.75, S 6.84; IR (KBr): $\tilde{\nu} = 3417$, 2972, 2364, 1615, 1596, 1573, 1560, 1491, 1446, 1358, 1261, 1170, 1085, 1032, 910, 844, 816, 762, 730, 705, 662, 618, 555, 522 cm^{-1}; molar conductivity (MeCN): $\Lambda_m = 441\ \Omega^{-1}\,cm^2\,mol^{-1}$. Vapour diffusion of diethyl ether into a solution of complex **24**·4H_2O in acetonitrile gave single crystals of $[Co^{II}_2(TsPMAT)_2](BF_4)_4$·6MeCN (**24**·6MeCN).

$[Fe^{II}_2(TsPMAT)_2](BF_4)_4$ (25): A colourless solution of $Fe(BF_4)_2$·6H_2O (68 mg, 0.20 mmol) in ethanol (10 mL) was added dropwise to a refluxing colourless solution of compound **14** (127 mg, 0.20 mmol) in ethanol (20 mL), and the resulting yellowish solution was refluxed for a further 30 min before it was allowed to cool to room temperature. The solvent volume was reduced to about one third of the original volume and the resulting solid was filtered off and washed with a little ethanol and diethyl ether. Drying in vacuo gave an air-sensitive cream-coloured powder (124 mg, 71 %) that quickly turned yellow-brown when exposed to air. On the basis of its elemental analysis this material was tentatively formulated as $[Fe^{II}_2(TsPMAT)_2](BF_4)_4$ (**25**). Elemental analysis calcd (%) for $C_{60}H_{64}B_4F_{16}Fe_2N_{16}O_8S_4$ (1724.42): C 41.79, H 3.74, N 13.00, S 7.44; found: C 42.58, H 4.20, N 13.51, S 6.96.

General procedure for $[M^{II}_2(PMAT)_2]X_4$ (26–30): A solution of $Mn(ClO_4)_2$·6H_2O or $M(BF_4)_2$·6H_2O (M = Fe, Co, Ni, Zn) (0.25 mmol) in acetonitrile (5 mL) was added dropwise to a colourless solution of compound **15** (81 mg, 0.25 mmol) in acetonitrile (10 mL). The mixture was stirred at room temperature for 1 h, during which time the product precipitated. The solid was filtered off and washed with acetonitrile and diethyl ether. Drying in vacuo gave the complexes as colourless (Mn, Zn) or pale-coloured (Fe, Co, Ni) powders.

$[Mn^{II}_2(PMAT)_2](ClO_4)_4$ (26): $Mn(ClO_4)_2$·6H_2O (90 mg) were used to obtain complex **26** (122 mg, 84 %) as a colourless powder. Elemental analysis calcd (%) for $C_{32}H_{40}Cl_4Mn_2N_{16}O_{16}$ (1156.46): C 33.24, H 3.49, N 19.38; found: C 33.54, H 3.28, N 19.40; IR (KBr): $\tilde{\nu} = 3152$, 2920, 1605, 1570, 1555, 1490, 1438, 1377, 1312, 1237, 1146, 1117, 1086, 1018, 908, 812, 765, 735, 627 cm^{-1}; molar conductivity (DMF): $\Lambda_m = 247\ \Omega^{-1}\,cm^2\,mol^{-1}$.

$[Fe^{II}_2(PMAT)_2](BF_4)_4$ (27):[31] $Fe(BF_4)_2$·6H_2O (84 mg) was used to obtain complex **27** (105 mg, 76 %) as a pale yellow powder. Elemental analysis calcd (%) for $C_{32}H_{40}B_4F_{16}Fe_2N_{16}$ (1107.69): C 34.70, H 3.64, N 20.23; found: C 34.68, H 3.50, N 19.89; IR (KBr): $\tilde{\nu} = 3125$, 2916, 1607, 1570, 1558, 1489, 1438, 1375, 1306, 1239, 1083, 1036, 891, 816, 766, 730, 668, 645, 538, 521, 467 cm^{-1}; molar conductivity (DMF): $\Lambda_m = 224\ \Omega^{-1}\,cm^2\,mol^{-1}$. Slow evaporation of an acetonitrile/*N*,*N*-dimethylformamide mixture containing the powder gave single crystals of $[Fe^{II}_2(PMAT)_2](BF_4)_4$·DMF (**27**·DMF).[31]

$[Co^{II}_2(PMAT)_2](BF_4)_4$ (28): $Co(BF_4)_2$·6H_2O (85 mg) was used to obtain complex **28** (113 mg, 81 %) as a pale purple powder. Elemental analysis calcd (%) for $C_{32}H_{40}B_4Co_2F_{16}N_{16}$ (1113.86): C 34.51, H 3.62, N 20.12; found: C 34.35, H 3.43, N 19.72; IR (KBr): $\tilde{\nu} = 3177$, 2919, 1608, 1569, 1562, 1490, 1439, 1374, 1308, 1241, 1083, 1034, 898, 814, 765, 731, 638, 533, 521, 470, 423, 413 cm^{-1}; molar conductivity (DMF): $\Lambda_m = 264\ \Omega^{-1}\,cm^2\,mol^{-1}$.

$[Ni^{II}_2(PMAT)_2](BF_4)_4$ (29): $Ni(BF_4)_2$·6H_2O (85 mg) was used to obtain complex **29** (39 mg, 28 %) as a pale lilac powder. Elemental analysis calcd (%) for $C_{32}H_{40}B_4F_{16}N_{16}Ni_2$ (1113.37): C 34.52, H 3.62, N 20.13; found: C 34.53, H 3.57, N 19.73; IR (KBr): $\tilde{\nu} = 3175$, 2918, 1608, 1571, 1490, 1441, 1374, 1306, 1242, 1083, 1035, 898, 817, 771, 730, 667, 642, 533, 521, 476, 429, 418 cm^{-1}; molar conductivity (DMF): $\Lambda_m = 241\ \Omega^{-1}\,cm^2\,mol^{-1}$.

$[Zn^{II}_2(PMAT)_2](BF_4)_4$ (30): $Zn(BF_4)_2$·6H_2O (87 mg) was used to obtain complex **30** (105 mg, 74 %) as a colourless powder. Elemental analysis calcd (%) for $C_{32}H_{40}B_4F_{16}N_{16}Zn_2$ (1126.75): C 34.11, H 3.58, N 19.89; found: C 33.79, H 3.33, N 19.89; IR (KBr): $\tilde{\nu} = 3171$, 2920, 1607, 1563, 1491, 1440, 1376, 1311, 1240, 1083, 1035, 909, 812, 767, 732, 636, 533, 522, 472 cm^{-1}; molar conductivity (DMF): $\Lambda_m = 231\ \Omega^{-1}\,cm^2\,mol^{-1}$.

Crystal data for $[Co^{II}_2(TsPMAT)_2](BF_4)_4$·6MeCN (24·6MeCN): $C_{72}H_{82}B_4Co_2F_{16}N_{22}O_8S_4$, $M_r = 1976.94$ g mol^{-1}, triclinic, space group $P\bar{1}$, $a = 12.9415(1)$, $b = 13.0630(2)$, $c = 14.1653(3)$ Å, $\alpha = 71.882(1)°$, $\beta = 83.338(1)°$, $\gamma = 70.329(1)°$, $V = 2142.98(6)$ Å^3, $\rho_{calcd} = 1.532$ g cm^{-3}, $T = 150(2)$ K, $Z = 1$, $F(000) = 1014$, $\mu = 0.587$ mm^{-1}. Brown prism, 0.22×0.16×0.08 mm^3; 17032 reflections collected in the range $1.51° < \theta < 24.00°$

($-14 \le h \le 14$, $-14 \le k \le 14$, $-16 \le l \le 16$), 6694 independent reflections. Final indices: $R1 = 0.0738$, $wR2 = 0.1830$ [$I > 2\sigma(I)$]; $R1 = 0.1243$, $wR2 = 0.2122$ (all data); GOF = 1.037; max/min residual electron density 1.287/ -0.608 e Å^{-3}. Data were collected on a Bruker SMART CCD area detector using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods with SHELXS-97[79,80] and refined against F^2 using all data by full-matrix least-squares techniques using SHELXL-97.[81] CCDC-265770 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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