

Probing the Dinucleating Behaviour of a Bis-Bidentate Ligand: Synthesis and Characterisation of Some Di- and Mononuclear Cobalt(II), Nickel(II), Copper(II) and Zinc(II) Complexes of 3,5-Di(2-pyridyl)-4-(1*H*-pyrrol-1-yl)-4*H*-1,2,4-triazole

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As a probe of the dinucleating ability of the known but little studied bis-bidentate ligand 3,5-di(2-pyridyl)-4-(1*H*-pyrrol-1-yl)-4*H*-1,2,4-triazole (pldpt) its reactivity towards $\text{MX}_2 \cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{Co}^{\text{II}}$, Ni^{II} and Zn^{II} ; $\text{X} = \text{ClO}_4^-$ and BF_4^-) as well as $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, in a 1:1 metal-to-ligand molar ratio in MeCN, has been investigated. In the case of Co^{II} , Ni^{II} and Zn^{II} , these reactions gave dinuclear complexes $\text{M}^{\text{II}}_2(\text{pldpt})_2 \cdot \text{X}_4(\text{MeCN})_m(\text{H}_2\text{O})_n$, whereas for Cu^{II} initially the mononuclear complex $[\text{Cu}^{\text{II}}(\text{pldpt})_2(\text{ClO}_4)_2]$ was isolated, followed by the dinuclear complex $[\text{Cu}^{\text{II}}_2(\text{pldpt})_2(\text{MeCN})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_4$. The use of the strongly polar aprotic co-solvent DMF resulted in the partial breakdown of the initial dinuclear entities in the case of Co^{II} and Ni^{II} but not in the case of Zn^{II} . In all five of the structurally characterised dinuclear complexes the $(\text{N}', \text{N}^1, \text{N}^2, \text{N}'')_2$ double-bridging coordination mode is realised with distorted octahedral N_4Y_2 -coordinated metal centres ($\text{Y} = \text{DMF}$, H_2O or MeCN). The two mononuclear complexes feature the common *trans*-(N', N^1)₂ coordination

mode with axial DMF or ClO_4^- co-ligands. The near-perpendicular orientation [$82.4(3)$ – $88.8(1)^\circ$] of the π -electron-rich 4-(1*H*-pyrrol-1-yl) substituent with respect to the triazole ring of pldpt, observed in all of these structures, means that no π -interactions are expected between these rings so any electronic interaction is likely to be small. Whether a di- or mononuclear complex of pldpt forms is therefore primarily determined by a number of other factors, including the reaction stoichiometry, the nature of the counterions and the solvent, as well as the relative solubility of the various possible products. Clearly the nature of the N^4 substituent can have a major impact on the last of these factors. Magnetic studies carried out on the dinuclear complexes revealed that the triazole bridges mediate relatively weak antiferromagnetic coupling between the two metal centres.

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Introduction

The utilisation of 1,2,4-triazole derivatives as bridging ligands in transition-metal complexes is currently of considerable interest.^[1–3] The 4-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles are bis-bidentate so they are potentially dinucleating ligands that should be capable of bridging two metal ions by means of the N_2 unit of the central triazole ring.^[2] Quite a large range of such ligands have been used for the preparation of transition-metal complexes (Figure 1). In the resulting di- and mononuclear complexes a variety of coordination modes have been observed of which

the dinuclear $(\text{N}', \text{N}^1, \text{N}^2, \text{N}'')_2$ double bridging and the mononuclear $(\text{N}', \text{N}^1)_2$ coordination mode are the most common and most important ones (Figure 2).^[2] For octahedral complexes featuring the latter mode, the *trans* type is frequently encountered. Here, the pyridine-triazole moieties of the two ligands are coordinated to the metal centre in a common plane with axially *trans*-positioned co-ligands. In contrast, there is only one example in the literature where the isomeric *cis* type is realised.^[4]

Within this ligand class the reactivity of 4-amino-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole (NH_2dpt , **2**) (Figure 1) towards transition-metal salts and the properties of the resulting di- and mononuclear complexes have been studied quite extensively over the last 20 years.^[5–29] From an electronic point of view the presence of the strongly electron-donating amino group on N^4 should facilitate the formation of dinuclear complexes of this ligand. However, of this family only two dinuclear complexes, namely $[\text{Ni}^{\text{II}}_2(\text{NH}_2\text{dpt})_2(\text{H}_2\text{O})_2\text{Cl}_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ ^[5] and $[\text{Cu}^{\text{II}}_2(\text{NH}_2\text{dpt})(\text{H}_2\text{O})_4(\text{SO}_4)_2] \cdot \text{H}_2\text{O}$,^[12] have been structurally characterised

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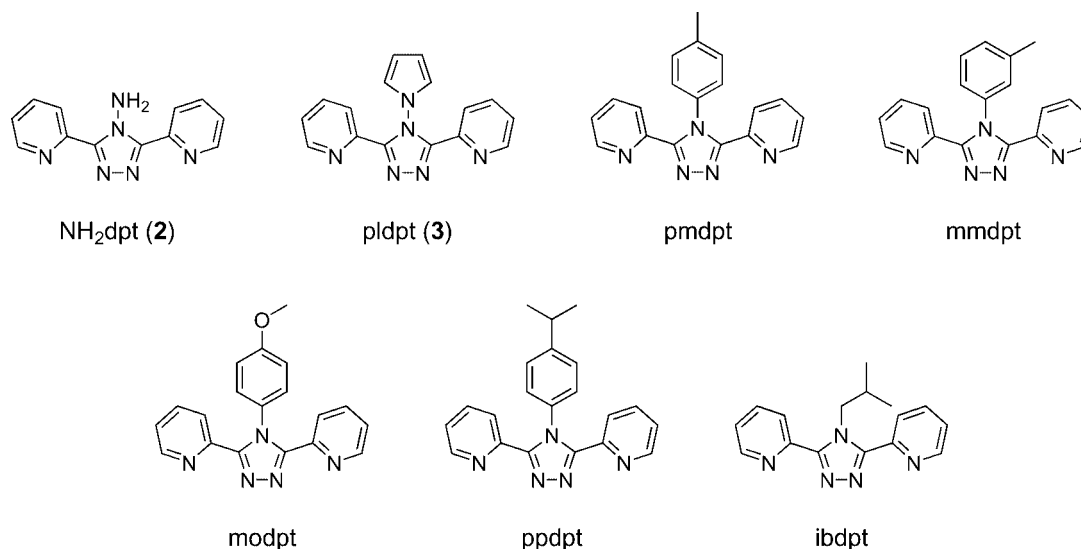


Figure 1. Structural drawings of the 4-substituted 3,5-di(2-pyridyl)-4H-1,2,4-triazoles that have been employed to date as ligands in coordination compounds.

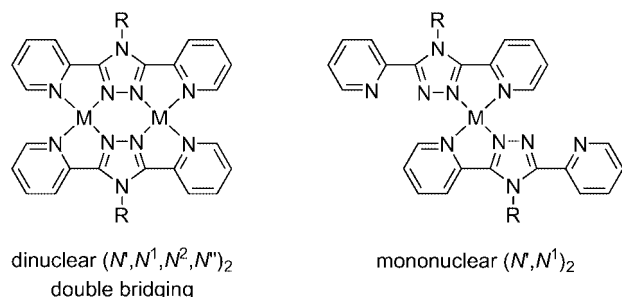


Figure 2. Schematic representation of the two most common coordination modes of 4-substituted 3,5-di(2-pyridyl)-4H-1,2,4-triazoles. In the actual complexes the metal centres can bind additional co-ligands according to the respective coordination geometries.

to date. 4-Isobutyl-3,5-di(2-pyridyl)-4H-1,2,4-triazole (ibdpt)^[30] (Figure 1), with its electron-donating alkyl substituent on N^4 , has also been found to afford both di- and mononuclear complexes.^[31–33] In contrast, the 4-aryl-3,5-di(2-pyridyl)-4H-1,2,4-triazoles have almost exclusively produced mononuclear complexes to date, in some cases despite the reaction being carried out with a metal-to-ligand molar ratio of 1:1.^[4,34–42] The first, and so far the only, dinuclear complex of a 4-aryl-3,5-di(2-pyridyl)-4H-1,2,4-triazole, namely a dinuclear silver(I) complex of 4-(4-isopropylphenyl)-3,5-di(2-pyridyl)-4H-1,2,4-triazole (ppdpt) (Figure 1) obtained from MeCN employing a 1:1 metal-to-ligand molar ratio, was reported very recently.^[43] Given that in these complexes the aryl substituents on N^4 form angles of about 68–84° with the triazole ring, no significant π -interactions are expected between them. Therefore, any electronic effect that the aryl substituent on N^4 might exert on the triazole ring must occur through the σ -bond framework so is likely to be small. There is only one report in the literature dealing with 3,5-di(2-pyridyl)-4-(1H-pyrrol-1-yl)-4H-1,2,4-triazole (pldpt, **3**) (Figure 1) and it describes the structural characterisation of the dinuclear complex $[\text{Co}^{\text{II}}_2$

(pldpt)₂(H₂O)₄]Cl₄·2MeOH·2H₂O, which was formed from the 1:1 reaction of CoCl₂·6H₂O and pldpt (**3**) in MeOH/H₂O, 4:1.^[44]

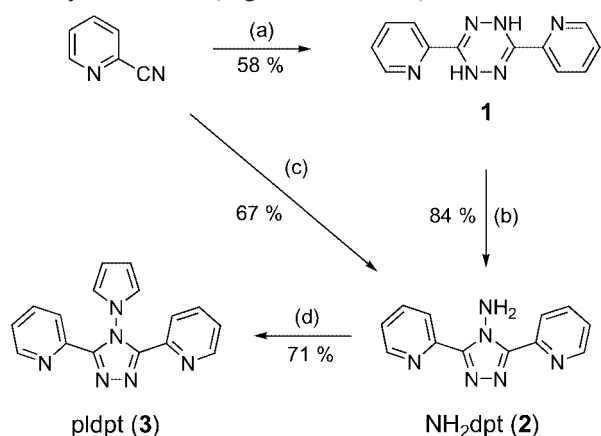
Overall it appears that the factors which combine to determine the nature of the products of such a complexation reaction, in particular whether a di- or mononuclear complex is formed as the main product, include the reaction stoichiometry, the choice of the counterions and the solvent used, as well as the influence of the N^4 substituent on the electronic structure and conformation of the respective ligand and on the relative solubility of the various possible product complexes. Systematic studies aimed at investigating the relative importance of these factors are currently lacking but clearly desirable so we are beginning to address this as part of our ongoing studies which are directed towards the synthesis and characterisation of dinuclear 1,2,4-triazole-bridged complexes of such ligands,^[2,3,30,32,33,45–51] with a particular interest in iron(II) complexes.^[52] Given that to date dinuclear 1,2,4-triazole-bridged complexes are far less common than the corresponding mononuclear complexes, here we target the controlled formation of further examples of dinuclear complexes of pldpt (**3**) by employing a metal-to-ligand molar ratio of 1:1 in the complexation reactions and varying the solvents and counterions.

Results and Discussion

Ligand Synthesis

Following the classic two-step procedure of Geldard and Lions,^[53] the condensation of 2-pyridinecarbonitrile with N₂H₄·H₂O gave 3,6-di(2-pyridyl)-1,4-dihydro-1,2,4,5-tetrazine (**1**) in 58% yield (Scheme 1). The subsequent rearrangement of the dihydrotetrazine **1** in 2 M HCl afforded NH₂dpt (**2**) in 84% yield.^[53] Alternatively, NH₂dpt (**2**) could be obtained directly from the two reactants by em-

ploying the one-pot procedure described by Lagrenée and co-workers (Scheme 1).^[54] However, it was found that the reaction was much slower than reported and difficult to drive to completion. The initial product thus obtained had to be recrystallised at least twice in order to obtain pure material. This caused the final yield of NH₂dpt (**2**) to drop significantly and the two-step procedure of Geldard and Lions^[53] was therefore preferred. The reaction of NH₂dpt (**2**) with 2,5-dimethoxytetrahydrofuran^[55,56] in AcOH/1,4-dioxane (1:1) readily gave pldpt (**3**) in 77% yield.^[44] Compounds **1–3** were fully characterised by spectroscopic methods. In addition, pldpt (**3**) was characterised by single-crystal X-ray diffraction (Figures S1 and S2).



Scheme 1. Synthesis of 3,5-di(2-pyridyl)-4-(1H-pyrrol-1-yl)-4H-1,2,4-triazole (pldpt, **3**). Reagents and conditions: (a) N₂H₄·H₂O, reflux; (b) 2 M HCl, reflux; (c) N₂H₄·H₂O, N₂H₄·H₂SO₄, 1,2-ethanediol, 130 °C; (d) 2,5-dimethoxytetrahydrofuran, AcOH, 1,4-dioxane, reflux.

There has been some confusion about the exact nature of the dihydrotetrazine intermediates arising from the condensation of nitriles with hydrazine. Especially in the older literature, including leading reviews on tetrazines and their dihydro derivatives^[57–59] as well as one on a related topic,^[60] these compounds are mostly considered to be the 1,2-tautomers. However, at least in the case of the condensation of 2-pyridinecarbonitrile with N₂H₄·H₂O, it has now been proven unequivocally by two independent research groups on the basis of single-crystal X-ray diffraction that the product of this reaction is in fact the 1,4-tautomer.^[61,62]

Synthesis of the Cobalt(II) Complexes

According to the literature, the reaction of pldpt (**3**) with CoCl₂·6H₂O in a 1:1 molar ratio in MeOH/H₂O (4:1) gives, on slow evaporation of the reaction mixture, orange crystals of [Co^{II}₂(pldpt)₂(H₂O)₄]Cl₄·2MeOH·2H₂O in 60–70% yield.^[44] Following this procedure as closely as possible, the synthesis of this material was attempted. However, instead of orange crystals, irregular beige crystals started to separate from the orange-brown solution after a few days. Over the course of four weeks the solution was allowed to evaporate almost completely forming even more of the beige material. On filtration and drying, the beige crystalline mate-

rial became dull which indicated the loss of some solvent. Visual examination of the resulting solid under a microscope showed that it contained a few tiny orange prisms, presumably of [Co^{II}₂(pldpt)₂(H₂O)₄]Cl₄·2MeOH·2H₂O. The small amount of orange product was separated physically from the bulk beige material but since it could not be obtained in sufficient material for an elemental analysis its presumed identity could not be verified. The elemental analysis of the beige solid was in good agreement with a mononuclear 1:2 complex with a composition of Co^{II}-(pldpt)₂Cl₂(solvent). These findings are in marked contrast to the results reported by Mandal and co-workers.^[44]

In the hope of getting a well-defined and less soluble solid product directly from the reaction mixture the reaction was subsequently carried out in neat EtOH instead of MeOH/H₂O (4:1). Thus, the reaction of pldpt (**3**) with CoCl₂·6H₂O in a 1:1 molar ratio at reflux resulted in the initial formation of a blue solid. After 15 minutes the reaction mixture was cooled and stirring the resulting suspension at room temperature for 24 hours caused the solid to turn pink, presumably due to slow co-ligand exchange of a kinetic product to form a thermodynamically more stable product. The elemental analysis of this pink solid was in good agreement with a dinuclear 2:2 complex with a composition of Co^{II}₂(pldpt)₂Cl₄(solvent). This material proved to be insoluble in all organic solvents, including DMF, MeNO₂ and DMSO, and could only be dissolved in H₂O. However, since all attempts to obtain a crystalline material from H₂O were unsuccessful, further purification and characterisation was not possible.

As a result of these disappointing findings using CoCl₂·6H₂O the coordination behaviour of pldpt (**3**) towards Co(ClO₄)₂·6H₂O was investigated next, in the hope of obtaining a solid product straight from the reaction mixture that would exhibit better solubility in organic solvents, thus allowing purification and proper characterisation. In order to achieve the formation of a dinuclear 2:2 complex, Co(ClO₄)₂·6H₂O was treated with pldpt (**3**) in a 1:1 molar ratio in MeCN. The resulting orange solid, which separated from the reaction mixture in ca. 90% yield, gave an elemental analysis in good agreement with a dinuclear 2:2 complex with a composition of Co^{II}₂(pldpt)₂(ClO₄)₄(MeCN)_{*m*}-(H₂O)_{*n*} (**4**). The solvent content of this material varied widely from batch to batch and the drying of samples at 60 °C in vacuo (CAUTION!) for several days similarly resulted in the formation of materials of variable solvent content. While complex **4** was only very sparingly soluble in MeCN, the addition of a little DMF led to dissolution. Vapour diffusion of Et₂O into a solution of complex **4** in MeCN/DMF (10:1) resulted in the formation of two different kinds of crystalline materials, namely orange prisms and yellow blocks, in variable relative amounts. Both species were studied by single-crystal X-ray diffraction. Thus, the orange crystals were identified as the dinuclear complex [Co^{II}₂(pldpt)₂(DMF)₂(H₂O)₂](ClO₄)₄·0.5Et₂O (**5**) (Figure 3) whereas the yellow crystals were found to be of the mononuclear complex [Co^{II}(pldpt)₂(DMF)₂](ClO₄)₂ (**6**) (Figure 4). These findings suggest that in the presence of DMF

the initial dinuclear complex **4** is unstable, resulting in the formation of a mixture of di- and mononuclear species, complexes **5** and **6**, respectively.

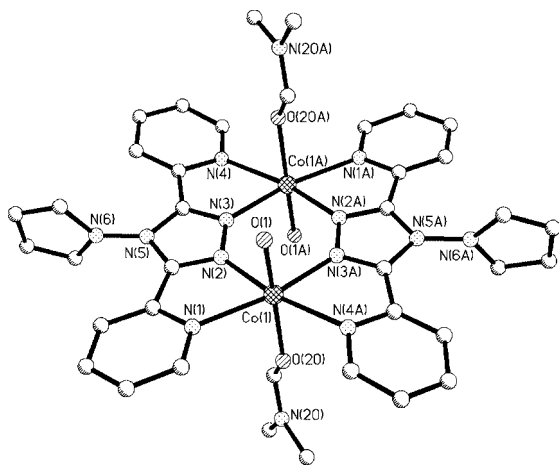


Figure 3. View of the molecular structure of the cation of $[\text{Co}^{\text{II}}_2(\text{pldpt})_2(\text{H}_2\text{O})_2(\text{DMF})_2](\text{ClO}_4)_4 \cdot 0.5\text{Et}_2\text{O}$ (**5**). Hydrogen atoms have been omitted for clarity. Symmetry operation used to generate equivalent atoms: (A) $-x + 1, -y + 1, -z + 2$.

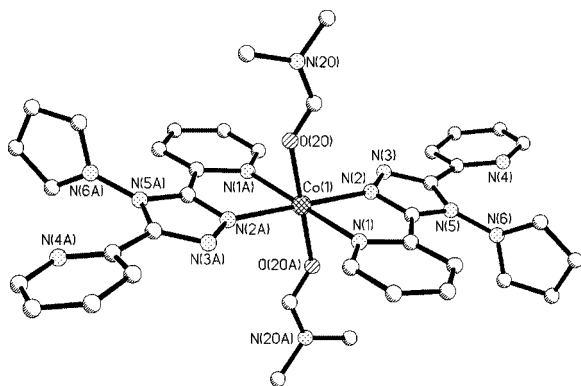


Figure 4. View of the molecular structure of the cation of $[\text{Co}^{\text{II}}(\text{pldpt})_2(\text{DMF})_2](\text{ClO}_4)_2$ (**6**). Hydrogen atoms have been omitted for clarity. Symmetry operation used to generate equivalent atoms: (A) $-x + 1, -y, -z$.

Faced with the need to use DMF as a co-solvent in order to dissolve the ClO_4^- complex **4** and the resulting formation of a mixture of species of different nuclearities, the synthesis of the BF_4^- analogue was carried out as this material was expected to exhibit better solubility in MeCN and therefore might not require the use of DMF. Thus, reacting $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ with pldpt (**3**) in a 1:1 molar ratio in MeCN afforded a pale orange powder, in ca. 80% yield, which had a composition of $\text{Co}^{\text{II}}_2(\text{pldpt})_2(\text{BF}_4)_4(\text{MeCN})_m(\text{H}_2\text{O})_n$ (**7**). As found earlier for the ClO_4^- analogue **4**, the solvent content of the material was variable and prolonged heating in vacuo afforded only partially desolvated materials of variable compositions. As anticipated, this complex could be readily redissolved in MeCN. Vapour diffusion of Et_2O into the MeCN mother liquor, or into a solution of complex **7** in MeCN, gave only one crystalline species which was identified as $[\text{Co}^{\text{II}}_2(\text{pldpt})_2(\text{MeCN})_2(\text{H}_2\text{O})_2](\text{BF}_4)_4$ (**8**) (Figure S3) by single-crystal X-ray diffraction. Thus, in MeCN

alone the initial dinuclear complex **7** is stable and is not broken down into a mixture of di- and mononuclear species.

Synthesis of the Nickel(II) Complexes

In parallel with the attempted synthesis of $[\text{Co}^{\text{II}}_2(\text{pldpt})_2(\text{H}_2\text{O})_4]\text{Cl}_4 \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$ [⁴⁴] the reaction of pldpt (**3**) with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in a 1:1 molar ratio under analogous conditions was examined. The slow evaporation of the olive-green $\text{MeOH}/\text{H}_2\text{O}$ (4:1) reaction mixture over the course of six weeks produced a mixture of a greenish crystalline solid and blue prisms in an estimated 3:1 ratio. As the physical separation of the two materials was practically impossible no analytical data for either of the compounds could be obtained. However, it is quite likely that, by analogy to the experiment employing $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ described above, a mixture of di- and mononuclear compounds was formed. Carrying out the reaction of pldpt (**3**) with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in a 1:1 molar ratio in EtOH instead of $\text{MeOH}/\text{H}_2\text{O}$ (4:1) gave a pale green solid which was subsequently identified, on the basis of its elemental analysis, as a dinuclear 2:2 complex with a composition of $\text{Ni}^{\text{II}}_2(\text{pldpt})_2\text{Cl}_4(\text{solvent})$. This material showed the same low solubility in organic solvents as the cobalt(II) analogue and this prevented its purification and further characterisation.

The reaction of pldpt (**3**) with $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in a 1:1 molar ratio in MeCN afforded $\text{Ni}^{\text{II}}_2(\text{pldpt})_2(\text{ClO}_4)_4(\text{MeCN})_m(\text{H}_2\text{O})_n$ (**9**) as a pale violet powder in ca. 80% yield. The solvent content of the initial powder was very variable. Once again prolonged heating in vacuo (CAUTION!) afforded materials of variable solvent content. As with the cobalt(II) analogue **4** the addition of a little DMF was necessary to dissolve the powder in MeCN. Vapour diffusion of Et_2O into a solution of complex **9** in MeCN/DMF (10:1) afforded an inseparable mixture of blue fern-like crystals and pink buttons, none of which were suitable for single-crystal X-ray diffraction studies. Here too, the use of DMF as a co-solvent has resulted in the formation of two different, presumably di- and mononuclear, species.

Employing $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ instead of the ClO_4^- salt in the 1:1 reaction with pldpt (**3**) in MeCN gave $\text{Ni}^{\text{II}}_2(\text{pldpt})_2(\text{BF}_4)_4(\text{MeCN})_m(\text{H}_2\text{O})_n$ (**10**) as a pale violet powder in ca. 40% yield and variable degrees of solvation. It could not be obtained in solvent-free form. As for the cobalt(II) analogues, this BF_4^- complex exhibited good solubility in neat MeCN, unlike its ClO_4^- analogue **9**. Vapour diffusion of Et_2O into a solution of complex **10** in MeCN or into the MeCN mother liquor of the initial powder afforded purple-blue prisms of $[\text{Ni}^{\text{II}}_2(\text{pldpt})_2(\text{MeCN})_4](\text{BF}_4)_4 \cdot 2\text{MeCN}$ (**11**) (Figure S4). Only one crystal type was observed so once again the initial dinuclear complex **10** is stable in MeCN.

Synthesis of the Copper(II) Complexes

The reaction of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with pldpt (**3**) in a 1:1 molar ratio in MeCN gave a sea-green solution from which

a blue powder separated after a few hours. This solid was identified as the mononuclear 1:2 complex $[\text{Cu}^{\text{II}}(\text{pldpt})_2(\text{ClO}_4)_2]$ (**12**) on the basis of its elemental analysis. Thus, the yield was subsequently calculated as 59%. Complex **12** could be readily dissolved in MeCN to give a blue solution. Vapour diffusion of Et_2O into this solution afforded blue single crystals of $[\text{Cu}^{\text{II}}(\text{pldpt})_2(\text{ClO}_4)_2] \cdot 2\text{DMF}$ (**13**) (Figure 5). While the origin of the DMF solvates in complex **13** could not be determined with absolute certainty it is likely that the glassware used was contaminated with DMF.

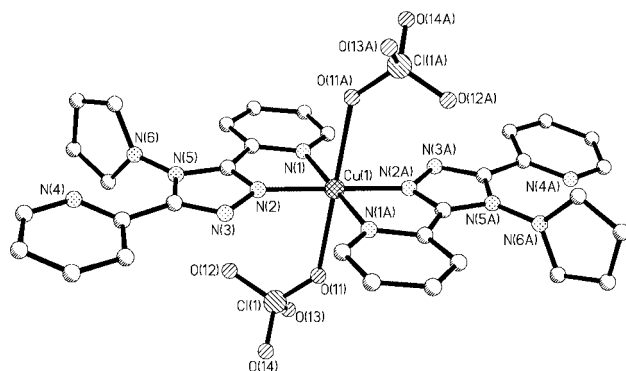


Figure 5. View of the molecular structure of $[\text{Cu}^{\text{II}}(\text{pldpt})_2(\text{ClO}_4)_2] \cdot 2\text{DMF}$ (**13**). Hydrogen atoms have been omitted for clarity. The DMF solvates are not shown. Symmetry operation used to generate equivalent atoms: (A) $-x, -y, -z + 1$.

Interestingly, the mother liquor remaining after filtering off the blue mononuclear complex **12**, now significantly enriched in Cu^{2+} ions relative to pldpt (**3**), retained its sea-green colour, suggesting the presence of a different species in solution. Subjecting this sea-green solution to vapour diffusion of Et_2O produced a small quantity of large green blocks. Single-crystal X-ray diffraction studies of these crystals revealed their dinuclear nature and led to the formulation of $[\text{Cu}^{\text{II}}_2(\text{pldpt})_2(\text{MeCN})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_4$ (**14**) (Figure 6).

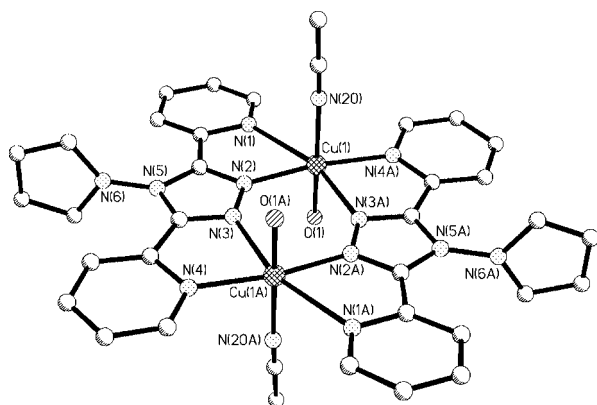


Figure 6. View of the molecular structure of the cation of $[\text{Cu}^{\text{II}}_2(\text{pldpt})_2(\text{H}_2\text{O})_2(\text{MeCN})_2](\text{ClO}_4)_4$ (**14**). Hydrogen atoms have been omitted for clarity. Symmetry operation used to generate equivalent atoms: (A) $-x + 2, -y + 1, -z + 1$.

It is noteworthy that of all the ClO_4^- complexes of pldpt (**3**) only the copper(II) complexes were readily soluble in neat MeCN. In addition, while in all other cases the initial

precipitates consisted of dinuclear species, in the case of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ the mononuclear complex $[\text{Cu}^{\text{II}}(\text{pldpt})_2(\text{ClO}_4)_2]$ (**12**) was the initial solid product despite the 1:1 metal-to-ligand molar ratio employed in the reaction.

Synthesis of the Zinc(II) Complexes

The reaction of pldpt (**3**) with $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in a 1:1 molar ratio in MeCN afforded $\text{Zn}^{\text{II}}_2(\text{pldpt})_2(\text{ClO}_4)_4 \cdot (\text{MeCN})_m(\text{H}_2\text{O})_n$ (**15**) as a colourless powder in ca. 80% yield. The solvent content of this material was variable and it could not be obtained in a solvent-free form even by heating it in vacuo (CAUTION!) for several days. Recrystallisation by vapour diffusion of Et_2O into a MeCN/DMF (10:1) solution of complex **15** gave colourless blocks and visually only one crystal type could be detected. Numerous attempts to grow single crystals by this method were made but only once could a poor X-ray data set be collected and this indicated that the crystals were of a dinuclear product. However, due to the very poor quality of the data, a complete analysis of the structure was not possible. Consistent with these findings, the elemental analysis of complex **15** clearly confirmed the 2:2 stoichiometry of this complex and the symmetrical NMR spectra obtained in $[\text{D}_7]\text{DMF}$ were also in agreement with the presence of only one species, specifically one with a symmetrical dinuclear architecture (see below). It is interesting to note that this dinuclear zinc(II) ClO_4^- complex does not form an equilibrium with a mononuclear species when it is dissolved in DMF as, if it did, this should be observed in the NMR spectra. This contrasts with the behaviour of the dinuclear cobalt(II) and nickel(II) ClO_4^- analogues, complexes **4** and **9**, respectively, which on recrystallisation from solutions containing DMF form mixtures of di- and mononuclear solid products. The relative amounts of these products present in solution are unknown.

In order to access better single crystals, our attention shifted from using the ClO_4^- salt to using the BF_4^- salt. Under the same conditions as employed for the preparation of the analogous BF_4^- complexes of cobalt(II) and nickel(II), complexes **7** and **10**, respectively, $\text{Zn}^{\text{II}}_2(\text{pldpt})_2(\text{BF}_4)_4 \cdot (\text{MeCN})_m(\text{H}_2\text{O})_n$ (**16**) was obtained from pldpt (**3**) and $\text{Zn}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, in ca. 60% yield, as a colourless powder. As with all complexes of pldpt (**3**) synthesised in this work, the solvent content of complex **16** varied considerably from batch to batch and the drying of samples at 60°C in vacuo for several days again resulted in materials of variable solvent content. Vapour diffusion of Et_2O into a solution of complex **16** in MeCN, or into its MeCN mother liquor, gave colourless blocks which were identified by single-crystal X-ray diffraction as the dinuclear complex $[\text{Zn}^{\text{II}}_2(\text{pldpt})_2(\text{MeCN})_2(\text{H}_2\text{O})_2](\text{BF}_4)_4$ (**17**) (Figure S5).

Description of the Structures

Single crystals of pldpt (**3**), in the form of colourless blocks, were obtained by slow evaporation of a solution of

the compound in EtOH. There are two crystallographically independent molecules in the asymmetric unit (Figures S1 and S2). The most noteworthy feature of this structure is the dissimilar orientation of the pairs of pyridine rings in the two molecules. While in the first molecule the pyridine nitrogen atoms point in opposite directions, both pyridine nitrogen atoms in the second molecule point away from the N₂ unit of the central five-membered heterocyclic ring. For the related ligand 2,5-di(2-pyridyl)-1,3,4-thiadiazole the latter conformation was recently calculated to be energetically favoured over the other two local minima forms with one or both pyridine nitrogen atoms pointing towards the N₂ unit.^[63] Indeed, an orientation of the pyridine rings with the nitrogen atoms pointing away from the N₂ unit of the central triazole ring is the only one previously observed in 4-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles^[30,37,64–73] and it is also the one usually adopted by non-coordinating pyridine rings in mononuclear 2:1 complexes incorporating such ligands.^[2] There are, in fact, only very few examples of complexes in the literature where the non-coordinated pyridine ring is reported to point away from the N⁴ substituent.^[13,40,42] The reason for the adoption of this unusual conformation for one of the two crystallographically independent molecules of pldpt (**3**) is difficult to pinpoint but presumably arises from a complex combination of weak π –

π and other packing effects. The conformation of the N(1)- and N(4)-pyridine rings was established by the differences in electron density for the two possible sites of the nitrogen atoms within the rings. This assignment was further supported by the fact that a hydrogen atom could only be located from the difference map at one of the two possible sites within the respective rings. Refinement of the structure with the alternative orientations was tried but was found to fit less well with the data.

In the dinuclear orange complex [Co^{II}₂(pldpt)₂(DMF)₂(H₂O)₂](ClO₄)₄·0.5Et₂O (**5**) (Figure 3) the (N',N¹,N²,N'')₂ double-bridging coordination mode (Figure 2) is realised. The two cobalt centres are 4.273(2) Å apart (Table 1) and in a distorted octahedral environment with a DMF and a H₂O molecule as axial co-ligands completing the coordination sphere (Table 2 and Table 3). While in this complex the normal situation of longer Co–N_{pyr} distances [2.235(5) and 2.244(5) Å] than Co–N_{trz} distances [2.085(5) and 2.098(4) Å] is again observed, the former are slightly longer than the corresponding distances observed in dinuclear cobalt(II) complexes of the related ligand 4-isobutyl-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole (ibdpt)^[32] and also slightly longer than those in the mononuclear complex [Co^{II}(pldpt)₂(DMF)₂](ClO₄)₂ (**6**) and the dinuclear complex [Co^{II}₂(pldpt)₂(MeCN)₂(H₂O)₂](BF₄)₄ (**8**) described below. Within

Table 1. Metal···metal distances [Å] in dinuclear complexes of 4-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles.

Complex	M···M ^[a]	Reference
[Co ^{II} ₂ (pldpt) ₂ (H ₂ O) ₄]Cl ₄ ·2MeOH·2H ₂ O	4.226(2)	[44]
[Co ^{II} ₂ (ibdpt) ₂ (MeCN) ₂ (H ₂ O) ₂](ClO ₄) ₄ (red-orange polymorph)	4.1481(7)	[32]
[Co ^{II} ₂ (ibdpt) ₂ (MeCN) ₂ (H ₂ O) ₂](ClO ₄) ₄ (yellow-orange polymorph)	4.1722(4)	[32]
[Co ^{II} ₂ (pldpt) ₂ (DMF) ₂ (H ₂ O) ₂](ClO ₄) ₄ ·0.5Et ₂ O (5)	4.273(2)	this work
[Co ^{II} ₂ (pldpt) ₂ (MeCN) ₂ (H ₂ O) ₂](BF ₄) ₄ (8)	4.2660(4)	this work
[Ni ^{II} ₂ (NH ₂ dpt) ₂ (H ₂ O) ₂ Cl ₂ ·4H ₂ O	4.1348(3)	[5]
[Ni ^{II} ₂ (ibdpt) ₂ (MeCN) ₄](ClO ₄) ₄	4.1107(9)	[32]
[Ni ^{II} ₂ (pldpt) ₂ (MeCN) ₄](BF ₄) ₄ ·2MeCN (11)	4.170(1)	this work
[Cu ^{II} ₂ (NH ₂ dpt)(H ₂ O) ₄ (SO ₄) ₂ ·H ₂ O	4.415(1)	[12]
[Cu ^{II} ₂ (ibdpt) ₂ (MeCN) ₂ (ClO ₄) ₂](ClO ₄) ₂ ·2MeCN	4.0701(10)	[32]
[Cu ^{II} ₂ (pldpt) ₂ (MeCN) ₂ (H ₂ O) ₂](ClO ₄) ₄ (14)	4.3140(5) [4.0861(9)]	this work
[Zn ^{II} ₂ (pldpt) ₂ (MeCN) ₂ (H ₂ O) ₂](BF ₄) ₄ (17)	4.455(2)	this work
[Ag ^I ₂ (ppdpt) ₂](ClO ₄) ₂ ·MeCN	4.367(4)	[43]

[a] Values in square brackets refer to the second molecule within the asymmetric unit.

Table 2. Selected distances [Å] for [Co^{II}₂(pldpt)₂(DMF)₂(H₂O)₂](ClO₄)₄·0.5Et₂O (**5**), [Co^{II}(pldpt)₂(DMF)₂](ClO₄)₂ (**6**), [Co^{II}₂(pldpt)₂(MeCN)₂(H₂O)₂](BF₄)₄ (**8**), [Ni^{II}₂(pldpt)₂(MeCN)₄](BF₄)₄·2MeCN (**11**), [Cu^{II}(pldpt)₂(ClO₄)₂·2DMF (**13**), [Cu^{II}₂(pldpt)₂(MeCN)₂(H₂O)₂](ClO₄)₄ (**14**) and [Zn^{II}₂(pldpt)₂(MeCN)₂(H₂O)₂](BF₄)₄ (**17**).

	5	6	8	13
M–N _{pyr}	Co(1)–N(1) 2.235(5) Co(1)–N(4A) 2.244(5)	Co(1)–N(1) 2.190(3)	Co(1)–N(1) 2.1876(12) Co(1)–N(4A) 2.2188(12)	Cu(1)–N(1) 2.034(2)
M–N _{trz}	Co(1)–N(2) 2.085(5) Co(1)–N(3A) 2.098(4)	Co(1)–N(2) 2.210(3)	Co(1)–N(2) 2.0976(12) Co(1)–N(3A) 2.0769(12)	Cu(1)–N(2) 1.979(2)
M–X	Co(1)–O(1) 2.052(4) Co(1)–O(20) 2.028(4)	Co(1)–O(20) 1.994(3)	Co(1)–N(20) 2.0876(12) Co(1)–O(1) 2.0464(11)	Cu(1)–O(11) 2.470(2)
	11		14	17
M–N _{pyr}	Ni(1)–N(1) 2.184(2) Ni(1)–N(7) 2.149(2)	Ni(2)–N(4) 2.165(2) Ni(2)–N(10) 2.171(2)	Cu(1)–N(1) 2.5170(18) Cu(1)–N(4A) 2.0264(17)	Zn(1)–N(1) 2.173(4) Zn(1)–N(4A) 2.227(4)
M–N _{trz}	Ni(1)–N(2) 2.026(2) Ni(1)–N(8) 2.038(2)	Ni(2)–N(3) 2.042(2) Ni(2)–N(9) 2.023(2)	Cu(1)–N(2) 1.9908(17) Cu(1)–N(3A) 2.2564(17)	Zn(1)–N(2) 2.164(4) Zn(1)–N(3A) 2.119(4)
M–X	Ni(1)–N(40) 2.025(2) Ni(1)–N(50) 2.031(2)	Ni(2)–N(60) 2.038(2) Ni(2)–N(70) 2.034(2)	Cu(1)–N(20) 2.0024(19) Cu(1)–O(1) 2.0029(16)	Zn(1)–N(20) 2.127(4) Zn(1)–O(1) 2.103(4)

Table 3. Selected angles [°] for [Co^{II}₂(pdppt)₂(DMF)₂(H₂O)₂](ClO₄)₄·0.5Et₂O (**5**), [Co^{II}(pdppt)₂(DMF)₂](ClO₄)₂ (**6**), [Co^{II}₂(pdppt)₂(MeCN)₂·(H₂O)₂](BF₄)₄ (**8**), [Ni^{II}₂(pdppt)₂(MeCN)₄](BF₄)₄·2MeCN (**11**), [Cu^{II}(pdppt)₂(ClO₄)₂·2DMF (**13**), [Cu^{II}₂(pdppt)₂(MeCN)₂(H₂O)₂](ClO₄)₄ (**14**) and [Zn^{II}₂(pdppt)₂(MeCN)₂(H₂O)₂](BF₄)₄ (**17**).

5		6		8	
N(1)–Co(1)–N(2)	74.21(18)	N(1)–Co(1)–N(2)	82.10(12)	N(1)–Co(1)–N(2)	75.13(4)
N(1)–Co(1)–N(3A)	166.98(18)	N(1)–Co(1)–N(1A)	180	N(1)–Co(1)–N(3A)	166.95(5)
N(1)–Co(1)–N(4A)	119.19(18)	N(1)–Co(1)–N(2A)	97.90(12)	N(1)–Co(1)–N(4A)	118.12(4)
N(1)–Co(1)–O(1)	86.61(17)	N(1)–Co(1)–O(20)	93.21(12)	N(1)–Co(1)–N(20)	87.89(4)
N(1)–Co(1)–O(20)	86.62(18)	N(1)–Co(1)–O(20A)	86.79(12)	N(1)–Co(1)–O(1)	86.60(4)
N(2)–Co(1)–N(3A)	92.78(17)	N(2)–Co(1)–N(2A)	180	N(2)–Co(1)–N(3A)	91.98(4)
N(2)–Co(1)–N(4A)	166.46(16)	N(2)–Co(1)–O(20)	107.24(11)	N(2)–Co(1)–N(4A)	166.41(4)
N(2)–Co(1)–O(1)	94.53(17)	N(2)–Co(1)–O(20A)	72.76(11)	N(2)–Co(1)–N(20)	93.56(5)
N(2)–Co(1)–O(20)	99.46(18)	O(20)–Co(1)–O(20A)	180	N(2)–Co(1)–O(1)	93.90(5)
N(3A)–Co(1)–N(4A)	73.82(17)			N(3A)–Co(1)–N(4A)	74.86(4)
N(3A)–Co(1)–O(1)	94.32(16)			N(3A)–Co(1)–N(20)	90.97(5)
N(3A)–Co(1)–O(20)	95.98(17)			N(3A)–Co(1)–O(1)	96.46(5)
N(4A)–Co(1)–O(1)	88.53(16)			N(4A)–Co(1)–N(20)	90.12(5)
N(4A)–Co(1)–O(20)	80.44(17)			N(4A)–Co(1)–O(1)	84.39(5)
O(1)–Co(1)–O(20)	162.17(18)			N(20)–Co(1)–O(1)	169.28(5)
11					
N(1)–Ni(1)–N(2)	76.21(9)	N(3)–Ni(2)–N(4)	76.25(9)		
N(1)–Ni(1)–N(7)	115.16(9)	N(3)–Ni(2)–N(9)	92.58(9)		
N(1)–Ni(1)–N(8)	168.53(9)	N(3)–Ni(2)–N(10)	168.75(9)		
N(1)–Ni(1)–N(40)	88.80(9)	N(3)–Ni(2)–N(60)	91.21(9)		
N(1)–Ni(1)–N(50)	87.74(9)	N(3)–Ni(2)–N(70)	90.09(9)		
N(2)–Ni(1)–N(7)	168.52(9)	N(4)–Ni(2)–N(9)	168.67(9)		
N(2)–Ni(1)–N(8)	92.34(9)	N(4)–Ni(2)–N(10)	114.89(9)		
N(2)–Ni(1)–N(40)	91.94(9)	N(4)–Ni(2)–N(60)	87.54(9)		
N(2)–Ni(1)–N(50)	91.49(9)	N(4)–Ni(2)–N(70)	91.29(9)		
N(7)–Ni(1)–N(8)	76.30(9)	N(9)–Ni(2)–N(10)	76.32(9)		
N(7)–Ni(1)–N(40)	86.97(9)	N(9)–Ni(2)–N(60)	90.83(9)		
N(7)–Ni(1)–N(50)	90.53(9)	N(9)–Ni(2)–N(70)	90.64(9)		
N(8)–Ni(1)–N(40)	92.44(9)	N(10)–Ni(2)–N(60)	90.84(9)		
N(8)–Ni(1)–N(50)	91.82(9)	N(10)–Ni(2)–N(70)	88.18(9)		
N(40)–Ni(1)–N(50)	174.42(9)	N(60)–Ni(2)–N(70)	177.99(9)		
13		14		17	
N(1)–Cu(1)–N(2)	80.85(9)	N(1)–Cu(1)–N(2)	70.77(6)	N(1)–Zn(1)–N(2)	75.47(14)
N(1)–Cu(1)–N(1A)	180	N(1)–Cu(1)–N(3A)	162.04(6)	N(1)–Zn(1)–N(3A)	163.75(14)
N(1)–Cu(1)–N(2A)	99.15(9)	N(1)–Cu(1)–N(4A)	120.03(7)	N(1)–Zn(1)–N(4A)	121.33(14)
N(1)–Cu(1)–O(11)	94.20(8)	N(1)–Cu(1)–N(20)	90.40(7)	N(1)–Zn(1)–N(20)	88.94(14)
N(1)–Cu(1)–O(11A)	85.80(8)	N(1)–Cu(1)–O(1)	81.71(7)	N(1)–Zn(1)–O(1)	86.17(15)
N(2)–Cu(1)–N(2A)	180	N(2)–Cu(1)–N(3A)	91.86(6)	N(2)–Zn(1)–N(3A)	88.35(14)
N(2)–Cu(1)–O(11)	86.33(8)	N(2)–Cu(1)–N(4A)	169.17(7)	N(2)–Zn(1)–N(4A)	162.70(14)
N(2)–Cu(1)–O(11A)	93.67(8)	N(2)–Cu(1)–N(20)	90.53(7)	N(2)–Zn(1)–N(20)	93.64(14)
O(11)–Cu(1)–O(11A)	180	N(2)–Cu(1)–O(1)	94.59(7)	N(2)–Zn(1)–O(1)	93.69(14)
		N(3A)–Cu(1)–N(4A)	77.31(7)	N(3A)–Zn(1)–N(4A)	74.91(14)
		N(3A)–Cu(1)–N(20)	94.39(7)	N(3A)–Zn(1)–N(20)	90.66(15)
		N(3A)–Cu(1)–O(1)	95.61(7)	N(3A)–Zn(1)–O(1)	96.50(14)
		N(4A)–Cu(1)–N(20)	90.21(7)	N(4A)–Zn(1)–N(20)	90.96(14)
		N(4A)–Cu(1)–O(1)	86.68(7)	N(4A)–Zn(1)–O(1)	84.06(14)
		N(20)–Cu(1)–O(1)	168.60(7)	N(20)–Zn(1)–O(1)	169.89(14)

the pyridine–triazole–pyridine moiety of complex **5** the N(4)–pyridine ring shows the largest twist, being inclined by 10.4(3)° relative to the triazole mean plane. The pyrrole ring intersects with the triazole mean plane at an angle of 82.4(3)° (Table 4). There are hydrogen bonds between the H₂O co-ligand and the two ClO₄[−] counterions [O(1)⋯O(11) 2.78 and O(1)⋯O(21) 2.84 Å].

The mononuclear yellow complex [Co^{II}(pdppt)₂(DMF)₂](ClO₄)₂ (**6**) (Figure 4) features the common *trans*-(*N'*,*N'*)₂ coordination mode (Figure 2). The coordination sphere about the cobalt centre is a strongly distorted octahedron with two DMF molecules in the axial positions (Table 2 and

Table 3). In this complex the Co–N_{pyr} distances are actually shorter than the Co–N_{trz} distances [2.189(3) and 2.209(3) Å, respectively], albeit only slightly, which is a geometrical feature that has not been observed previously in complexes of any 4-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazole. In complexes of this ligand type the M–N_{pyr} distances are usually longer, often significantly, than the M–N_{trz} distances.^[2] In addition, both the Co–N_{pyr} and the Co–N_{trz} distances are unusually long compared to those observed in related systems [2.102(4)–2.147(3) and 2.052(4)–2.124(2) Å, respectively].^[36,37,42] As is normal, the nitrogen atom of the non-coordinated pyridine ring points towards

Table 4. Angles [°] between the mean planes of central triazole ring and the attached pyridine and pyrrole rings in 3,5-di(2-pyridyl)-4-(1*H*-pyrrol-1-yl)-4*H*-1,2,4-triazole (pldpt, **3**) and its complexes.

Compound	N(1)-pyridine ^[a]	N(4)-pyridine ^[a]	N(6)-pyrrole ^[a]
pldpt (3)	31.1(1) [17.9(1)]	36.8(1) [29.2(1)]	82.4(1) [81.9(1)]
[Co ^{II} ₂ (pldpt) ₂ (DMF) ₂ (H ₂ O) ₂](ClO ₄) ₄ ·0.5Et ₂ O (5)	6.7(4)	10.4(3)	82.4(3)
[Co ^{II} (pldpt) ₂ (DMF) ₂](ClO ₄) ₂ (6)	6.2(2)	24.7(2)	87.4(1)
[Co ^{II} ₂ (pldpt) ₂ (MeCN) ₂ (H ₂ O) ₂](BF ₄) ₄ (8)	4.7(1)	5.6(1)	88.2(1)
[Ni ^{II} ₂ (pldpt) ₂ (MeCN) ₄](BF ₄) ₄ ·2MeCN (11)	7.7(2)	4.1(2)	88.0(1)
[Cu ^{II} (pldpt) ₂ (ClO ₄) ₂ ·2DMF (13)	3.8(2)	8.2(1)	85.3(1)
[Cu ^{II} ₂ (pldpt) ₂ (MeCN) ₂ (H ₂ O) ₂](ClO ₄) ₄ (14)	4.4(1)	4.7(1)	88.8(1)
[Zn ^{II} ₂ (pldpt) ₂ (MeCN) ₂ (H ₂ O) ₂](BF ₄) ₄ (17)	5.2(3)	5.5(3)	88.4(2)

[a] Values in square brackets refer to the N(7)-pyridine, N(10)-pyridine and N(12)-pyrrole rings of the second ligand molecule within the asymmetric unit.

the pyrrole ring which intersects with the triazole mean plane at an angle of 87.4(1)°. The N(1)- and N(4)-pyridine rings are tilted by 6.1(2)° and 24.7(2)°, respectively, relative to the triazole mean plane (Table 4).

The overall architecture of the dinuclear orange complex [Co^{II}₂(pldpt)₂(MeCN)₂(H₂O)₂](BF₄)₄ (**8**) (Figure S3) is very similar to that of the corresponding ClO₄[−] complex **5** described above. Here, the (N',N¹,N²,N'')₂ double-bridging coordination mode (Figure 2) is realised with a MeCN molecule being the second axial co-ligand, instead of DMF, in addition to the H₂O molecule which forms hydrogen bonds to the two BF₄[−] counterions [O(1)⋯F(11) 2.72 and O(1)⋯F(21) 2.73 Å]. The usual situation of longer Co–N_{pyr} distances [2.1876(12) and 2.2188(12) Å] than Co–N_{trz} distances [2.0769(12) and 2.0976(12) Å] is again observed (Table 2 and Table 3). The distance between the two cobalt centres of 4.2660(4) Å is almost identical to the value observed for the ClO₄[−] complex **5** (Table 1). The pyridine–triazole–pyridine moiety is almost perfectly planar [4.7(1) and 5.6(1)°] while the pyrrole ring is practically perpendicular [88.2(1)°] to the triazole mean plane (Table 4).

The dinuclear (N',N¹,N²,N'')₂ double-bridging coordination mode (Figure 2) is also featured in the purple-blue complex [Ni^{II}₂(pldpt)₂(MeCN)₄](BF₄)₄·2MeCN (**11**) (Figure S4). Here, each of the two nickel centres binds two MeCN co-ligands in the axial positions resulting in distorted octahedral N₆ coordination environments (Table 2 and Table 3). The distance of 4.170(1) Å between the two nickel centres is somewhat larger than the distances observed in other nickel(II) complexes of related ligands (Table 1).^[5,32] The Ni–N_{pyr} and Ni–N_{trz} distances of 2.149(2)–2.184(2) and 2.023(2)–2.042(2) Å, respectively, in complex **11** are in the same range as those observed in related complexes.^[5,32] The four Ni–N_{MeCN} distances are all very similar and within the range of 2.025(2)–2.038(2) Å. In both ligand molecules the pyridine–triazole–pyridine moiety is almost flat [7.7(2) and 4.1(2)°] while the respective pyrrole rings are virtually perpendicular [88.0(1)°] to the triazole mean plane (Table 4).

The copper centre in [Cu^{II}(pldpt)₂(ClO₄)₂·2DMF (**13**) (Figure 5) is octahedrally N₄O₂ coordinated with two molecules of pldpt (**3**) occupying the equatorial positions and two ClO₄[−] ions being bound axially, giving rise to the *trans*-(N',N¹)₂ coordination mode (Figure 2). Thus, the overall

architecture of complex **13** is the same as in [Cu^{II}(pyppt)₂(ClO₄)₂·MeCN,^[49] [Cu^{II}(ibdppt)₂(ClO₄)₂]^[32] and [Cu^{II}(pmdpt)₂(ClO₄)₂]^[41] with the Cu–N_{pyr}, Cu–N_{trz} and Cu–O distances [2.034(2), 1.979(2) and 2.470(2) Å, respectively] (Table 2 and Table 3) having very similar values as the corresponding distances observed in these related complexes [2.038(3)–2.045(2), 1.962(3)–1.989(2) and 2.466(3)–2.471(3) Å, respectively]. Both the coordinated and the non-coordinated pyridine rings show only slight deviations from planarity [3.8(2) and 8.2(1)°, respectively] with respect to the triazole mean plane. The pyrrole ring is almost perpendicular [85.3(1)°] to the triazole mean plane (Table 4).

In all of the previous structures of dinuclear complexes of 4-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles featuring the dinuclear (N',N¹,N²,N'')₂ double-bridging coordination mode (Figure 2), described in this paper and elsewhere,^[5,32,43,44] the two ligand molecules have been found to be in practically perfect alignment with each other, i.e. with the four nitrogen atoms of the bridging N₂ units of the two triazole moieties forming a rectangle. In contrast, in [Cu^{II}₂(pldpt)₂(MeCN)₂(H₂O)₂](ClO₄)₄ (**14**) (Figure 6) the two ligand molecules are offset sideways from one another, i.e. with the four nitrogen atoms of the bridging N₂ units of the two triazole moieties forming a parallelogram with acute angles of about 78°, resulting in a pronounced tetragonal distortion of the copper(II) centres. The consequences with regard to the distances between the two equivalent copper centres and their donor atoms are quite dramatic. The Cu–N_{pyr} and Cu–N_{trz} distances in complex **14** are the longest observed for any complex of a ligand featuring the bidentate pyridine–triazole moiety. The two Cu–N_{pyr} distances are markedly different from each other [2.5170(18) and 2.0264(17) Å] as are the two Cu–N_{trz} distances [1.9908(17) and 2.2564(17) Å] (Table 2 and Table 3). These geometrical features are a manifestation of an unsymmetrical Jahn–Teller elongation of the distorted CuN₅O coordination octahedron along the N(1)–Cu(1)–N(3A) axis [Cu(1)–N(1) 2.5170(18) and Cu(1)–N(3A) 2.2564(17) Å]. The Cu(1)–N(20) and the Cu(1)–O(1) distances between the metal centre and the axial MeCN and H₂O co-ligands, respectively, are practically identical [2.0024(19) and 2.0029(16) Å]. In contrast, in [Cu^{II}(pldpt)₂(ClO₄)₂·2DMF (**13**) (see above) as well as in analogous copper(II) complexes of related ligands the Jahn–Teller elongation of the

coordination octahedron occurs along the $X_{\text{axial}}\text{--Cu--}X_{\text{axial}}$ axis and is symmetrical. The distance of 4.3140(5) Å between the two copper centres in complex **14** is in between the corresponding distances observed in $[\text{Cu}^{\text{II}}_2(\text{NH}_2\text{dpt})(\text{H}_2\text{O})_4(\text{SO}_4)_2\cdot\text{H}_2\text{O}]^{12}$ and $[\text{Cu}^{\text{II}}_2(\text{ibdpt})_2(\text{MeCN})_2(\text{ClO}_4)_2](\text{ClO}_4)_2\cdot 2\text{MeCN}^{132}$ (Table 1). The axial H_2O co-ligand is involved in hydrogen bonding to the two ClO_4^- counterions [$\text{O}(1)\cdots\text{O}(11)$ 2.78 and $\text{O}(1)\cdots\text{O}(21)$ 2.81 Å]. Here too, the pyridine–triazole–pyridine moiety is nearly planar [4.4(1) and 4.7(1)°], with the pyrrole ring intersecting the triazole mean plane almost at 88.8(1)° (Table 4).

The molecular structure of $[\text{Zn}^{\text{II}}_2(\text{pldpt})_2(\text{MeCN})_2(\text{H}_2\text{O})_2](\text{BF}_4)_4$ (**17**) (Figure S5) is basically the same as that of the cobalt(II) analogue $[\text{Co}^{\text{II}}_2(\text{pldpt})_2(\text{MeCN})_2(\text{H}_2\text{O})_2](\text{BF}_4)_4$ (**8**) (Figure S3). Complex **17** is the first dinuclear zinc(II) complex of any 4-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazole to be synthesised and structurally characterised. The two zinc centres are separated by 4.455(2) Å (Table 1) and the pyridine–triazole–pyridine moiety shows only a slight deviation from planarity [5.2(3) and 5.5(3)°], while the pyrrole ring is almost perpendicular [88.4(2)°] to the triazole mean plane (Table 4). The complex adopts the dinuclear (N',N^1,N^2,N'')₂ double-bridging coordination mode (Figure 2). Here too, the two ligand molecules are somewhat shifted sideways relative to each other resulting in a slight tetragonal distortion of the system which is manifested in the relatively large variation of the $\text{Zn--N}_{\text{pyr}}$ and $\text{Zn--N}_{\text{triaz}}$ distances [2.173(4)–2.227(4) and 2.119(4)–2.164(4) Å, respectively] (Table 2 and Table 3). The H_2O co-ligand forms hydrogen bonds to the two BF_4^- counterions [$\text{O}(1)\cdots\text{F}(11)$ 2.75 and $\text{O}(1)\cdots\text{F}(21)$ 2.77 Å].

In all of the complexes of pldpt (**3**) synthesised and structurally characterised in the course of this work the mean planes of the central triazole ring and the π -electron-rich pyrrole ring of the ligand are not co-planar but rather intersect at almost right angles [82.4(3)–88.8(1)°] (Table 4). This precludes an electronic interaction occurring between them by a π -pathway. Therefore, if there is any transmission of electron density between these two heterocyclic rings it must occur across the σ -bond between them. Consequently, it is likely to be small.

Mass Spectrometry

ESI mass spectra were recorded in MeCN for all of the initial powdery complexes. In all of the spectra the parent peak was assigned to the species $[(\text{pldpt}) + \text{H}]^+$. The spectra of the dinuclear ClO_4^- complexes **4**, **9** and **15** showed, almost exclusively, peaks that were assigned to mononuclear species, including the fragments $[\text{M}(\text{pldpt})_3]^{2+}$ at $m/z = 461.7$ ($\text{M} = \text{Co}^{\text{II}}$), 461.1 ($\text{M} = \text{Ni}^{\text{II}}$) and 464.3 ($\text{M} = \text{Zn}^{\text{II}}$), respectively, with a metal-to-ligand molar ratio of 1:3 which has not been observed for complexes of any 4-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazole in the solid state so far. As the only peaks assignable to dinuclear species, the three spectra also had in common peaks for the fragments

$[\text{M}_2(\text{pldpt})_2(\text{ClO}_4)_3]^+$ at $m/z = 993.3$ ($\text{M} = \text{Co}^{\text{II}}$), 991.2 ($\text{M} = \text{Ni}^{\text{II}}$) and 1003.1 ($\text{M} = \text{Zn}^{\text{II}}$), respectively.

Despite their good solubility in MeCN, and the fact that only one dinuclear solid state species was formed in each case on crystallisation, the ESI mass spectra of the BF_4^- complexes **7**, **10** and **16** were not particularly informative and showed only about half the number of assignable peaks that the analogous ClO_4^- complexes had. As was the case with the ClO_4^- analogues, the spectra of complexes **7**, **10** and **16** all had peaks for the fragments $[\text{M}(\text{pldpt})_3]^{2+}$ in common, while no peaks corresponding to dinuclear species were observed for these compounds.

The ESI mass spectrum of $[\text{Cu}^{\text{II}}(\text{pldpt})_2(\text{ClO}_4)_2]$ (**12**) was in full agreement with the other analytical data of this complex, albeit that most of the peaks were assigned to copper(I) rather than copper(II) species, the former arising from reduction of the metal centre under the conditions of the experiment.

NMR Spectroscopy

The ^1H NMR spectrum of the dinuclear zinc(II) ClO_4^- complex **15** in $[\text{D}_7]\text{DMF}$ showed only six signals in the aromatic region, which was in agreement with only one species being present (Figure S6). This confirmed that this complex does not exist in an equilibrium with mononuclear species in DMF solution but retains its symmetrical dinuclear architecture in this solvent, in contrast to the recrystallisation behaviour of the analogous cobalt(II) and nickel(II) complexes **4** and **9**, respectively, in the presence of this solvent. Five of the signals were well resolved and only the signal at $\delta = 7.55$ ppm, which was assigned to 3-PyH, was broad. While the other five signals were shifted downfield, as could be expected upon coordination, by 0.12–0.23 ppm relative to the signals of free pldpt (**3**) in $[\text{D}_7]\text{DMF}$, the signal for 3-PyH was shifted upfield by 0.40 ppm, thus swapping places with the signal for 5-PyH. The single-crystal X-ray structure analysis of the analogous BF_4^- complex **17** shows that the pyrrole ring is, as expected on steric grounds, almost perpendicular to the two pyridine rings and the triazole ring in the solid state. The significant upfield shift of the signal for 3-PyH observed in the ^1H NMR spectra of both the ClO_4^- complex **15** and the BF_4^- complex **16** (see below) in $[\text{D}_7]\text{DMF}$ indicates that the same relative orientation is adopted in solution, as this proton appears to be interacting with the π -electron system of the adjacent pyrrole ring. As outlined above, the normal conformation of the pyridine rings in non-coordinated 4-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles is the one where the nitrogen atoms of the pyridine rings point towards the face of the pyrrole ring, i.e. the pyrrole ring is almost at a right angle to the triazole ring in all of the structurally characterised compounds, whereas on coordination in a dinuclear complex the pyridine rings are held the other way round due to the binding of the metal ions, so the 3-PyH protons now point towards the face of the pyrrole ring. For complex **17** the two independent distances between the 3-PyH and

the centroid of the pyrrole ring are 3.02 and 3.66 Å in the solid state. Finally, given that in the dinuclear complex the coordinated pyridine and triazole rings are expected to be approximately co-planar, these NMR spectroscopic data in $[D_7]DMF$ are consistent with the triazole and pyrrole rings being almost perpendicular to one another, precluding an electronic interaction occurring between them by a π -pathway and indicating that any electronic interactions occur via the N–N σ -bond.

The ^{13}C NMR spectrum of the dinuclear zinc(II) ClO_4^- complex **15** in $[D_7]DMF$, which was very similar to the corresponding spectrum of $pdppt$ (**3**) with all of the signals being shifted only slightly (Figure S7), was also consistent with the formulation of a dinuclear solution species and with only one species being present in DMF solution.

As expected, the NMR spectra, recorded in $[D_7]DMF$, of the dinuclear zinc(II) BF_4^- complex **16**, which upon recrystallisation from MeCN/Et₂O afforded the structurally characterised dinuclear complex **17** (see above), were practically identical to those observed for the analogous ClO_4^- complex **15**. Attempts were also made to record NMR spectra of complex **16** in $[D_3]MeCN$ for comparison but for unknown reasons this failed and useful spectral information could not be obtained using this solvent.

Conductivity Measurements

The molar conductivities of the ClO_4^- complexes **4**, **9** and **15** were determined in DMF. The values obtained (260, 300 and 255 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$, respectively) are in agreement with the expected value of about 240–300 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ for a 4:1 electrolyte in this solvent.^[74] For the BF_4^- complexes **7**, **10** and **16** the corresponding values, determined in DMF, were found to be 280, 250 and 270 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$, respectively, which are also within the expected range. Likewise,

the molar conductivities of complexes **7**, **10** and **16** in MeCN (480, 470 and 475 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$, respectively) were found to be in good agreement with the expected value of about 420–500 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ for 4:1 electrolytes in this solvent.^[74] The molar conductivity of the mononuclear copper(II) complex **12** was determined as 245 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ in MeCN. This value agrees well with that expected for a 2:1 electrolyte in MeCN (220–300 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$).^[74]

Magnetic Studies

Magnetic measurements were carried out on powder samples of the two dinuclear cobalt complexes $Co^{II}_2(pdppt)_2(ClO_4)_4(MeCN)_m(H_2O)_n$ (**4**) and $Co^{II}_2(pdppt)_2(BF_4)_4(MeCN)_m(H_2O)_n$ (**7**) as well as of the two dinuclear nickel complexes $Ni^{II}_2(pdppt)_2(ClO_4)_4(MeCN)_m(H_2O)_n$ (**9**) and $Ni^{II}_2(pdppt)_2(BF_4)_4(MeCN)_m(H_2O)_n$ (**10**), revealing in each case weak antiferromagnetic coupling between the metal centres (Table 6).

The dinuclear cobalt(II) complexes **4** and **7** exhibited almost identical magnetic behaviour despite the different counterions, thus indicating that the nature of the latter has practically no influence on the magnetism of these compounds. Similarly, the magnetic behaviour of different samples of the same compound was found to be independent within experimental error from the actual solvent content. The magnetic moments for complexes **4** (Figure 5) and **7** (Figure S7) at room temperature were 4.50 and 4.29 μ_B per cobalt(II) centre, respectively, and thus somewhat higher than for spin-only d^7 high-spin systems as a result of spin-orbit coupling and ligand field splitting effects acting on the $^4T_{1g}$ single ion states. For both complexes the fitted curves for the temperature dependence of the molar magnetic susceptibility showed a maximum, at $T = 13$ K with $\chi_m = 0.06806$ $cm^3\cdot mol^{-1}$ for complex **4** (Figure 7) and with

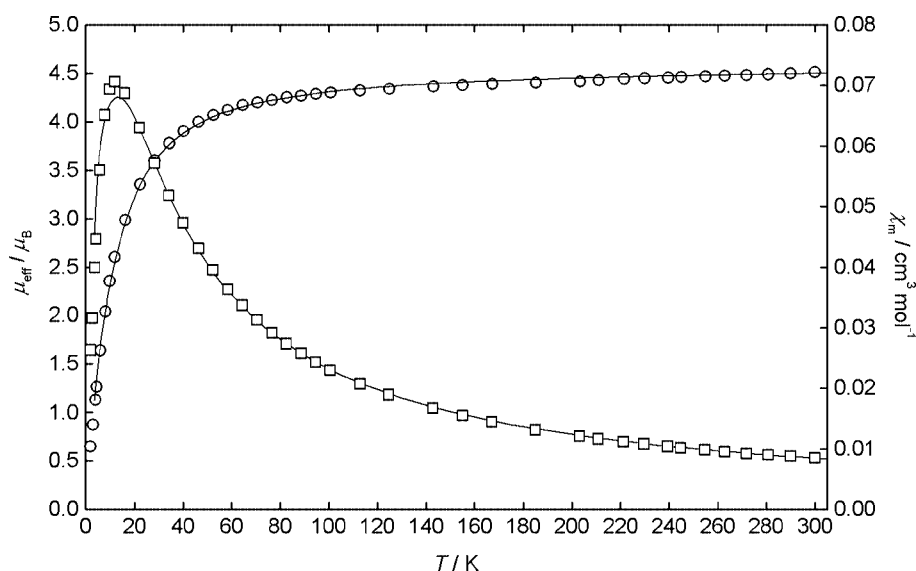


Figure 7. Temperature dependence of the effective magnetic moment μ_{eff} (○) and the molar magnetic susceptibility χ_m (□) per cobalt(II) centre for $Co^{II}_2(pdppt)_2(ClO_4)_4(MeCN)_m(H_2O)_n$ (**4**) ($m = 1$, $n = 0$). The solid lines represent the best fit using the parameters given in Table 5.

$\chi_m = 0.06166 \text{ cm}^3 \cdot \text{mol}^{-1}$ for complex **7** (Figure S8), a feature typical for antiferromagnetic exchange coupling. The magnetic data were fitted well by an $S = 3/2$ dimer model of the spin-only Heisenberg–Van Vleck type $(-2J\mathbf{S}_1 \cdot \mathbf{S}_2)^{[75]}$ indicating that orbital degeneracy had largely been removed. The best fit parameters are given in Table 5. The magnitude of the coupling between the two cobalt(II) centres in the ClO_4^- complex **4** ($J = -3.1 \text{ cm}^{-1}$) and the BF_4^- complex **7** ($J = -3.1 \text{ cm}^{-1}$) was similar to the corresponding value observed for $[\text{Co}^{\text{II}}_2(\text{TsPMAT})_2](\text{BF}_4)_4 \cdot 4\text{H}_2\text{O}$ ($J = -3.3 \text{ cm}^{-1}$)^[51] and was only slightly less than that reported for related complexes of other 4-substituted 3,5-di(2-pyridyl)-4H-1,2,4-triazoles.^[5,32]

Table 5. Magnetic data for $\text{Co}^{\text{II}}_2(\text{pldpt})_2(\text{ClO}_4)_4(\text{MeCN})_m(\text{H}_2\text{O})_n$ (**4**), $\text{Co}^{\text{II}}_2(\text{pldpt})_2(\text{BF}_4)_4(\text{MeCN})_m(\text{H}_2\text{O})_n$ (**7**), $\text{Ni}^{\text{II}}_2(\text{pldpt})_2(\text{ClO}_4)_4(\text{MeCN})_m(\text{H}_2\text{O})_n$ (**9**) and $\text{Ni}^{\text{II}}_2(\text{pldpt})_2(\text{BF}_4)_4(\text{MeCN})_m(\text{H}_2\text{O})_n$ (**10**).

Complex	<i>m</i>	<i>n</i>	<i>J</i> [cm^{-1}]	<i>g</i>	<i>TIP</i> [$\text{cm}^3 \cdot \text{mol}^{-1}$]	Monomer [%]
4	1	0	−3.1	2.36	$60 \cdot 10^{-6}$	0.1
7	1	2	−3.1	2.25	$65 \cdot 10^{-6}$	0.4
9	0	0	−8.8	2.05	0	0.5
10	0	4	−7.8	2.15	$65 \cdot 10^{-6}$	0.5

The room temperature effective magnetic moment of $2.82 \mu_B$ per nickel(II) centre for the ClO_4^- complex **9** (Figure 8) was reduced from the typical uncoupled value of ca. $3.1 \mu_B$ thus indicating that antiferromagnetic coupling was occurring. For the BF_4^- complex **10** the corresponding value was $3.00 \mu_B$ (Figure S9) and hence the nickel(II) centres are less strongly coupled than in complex **9**. The fitted curves for the temperature dependence of the molar magnetic susceptibility of complexes **9** (Figure 8) and **10** (Figure S9) had maxima at $T = 26 \text{ K}$ with $\chi_m = 0.01639 \text{ cm}^3 \cdot \text{mol}^{-1}$ and $T = 22 \text{ K}$ with $\chi_m = 0.02058 \text{ cm}^3 \cdot \text{mol}^{-1}$, respectively. The antiferromagnetic coupling between the two nickel(II) centres in the ClO_4^-

complex **9** was somewhat larger than in the BF_4^- complex **10**, the coupling constants being -8.8 and -7.8 cm^{-1} , respectively. Here too, the magnetic behaviour of different samples of the same compound was found to be independent within experimental error from the actual solvent content. As with the cobalt(II) complexes of this ligand described above, the antiferromagnetic coupling in complexes **9** and **10** was less than that observed in related nickel(II) complexes of other 4-substituted 3,5-di(2-pyridyl)-4H-1,2,4-triazoles.^[5,32]

Conclusion

The coordination behaviour of the known ligand pldpt (**3**)^[44] towards the first-row transition-metal ions Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} in reactions with a metal-to-ligand molar ratio of 1:1 has been investigated in detail for the first time. From these studies it is clear that this ligand can act as a bis-bidentate chelator and thus form dinuclear complexes but it has also been revealed that its dinuclear complexes can be labile in solution depending on the solvent used. Although in most cases the initial precipitates are dinuclear, equilibria between di- and mononuclear species can occur in solution, depending on the metal salt and the solvent employed. Thus, for example, the strongly polar aprotic solvent DMF causes the dinuclear cobalt(II) and nickel(II) ClO_4^- complexes **4** and **9**, respectively, to break up to some extent giving rise to mixtures of di- and mononuclear species, while the corresponding dinuclear zinc(II) ClO_4^- complex **15** appears to be perfectly stable in this solvent. In contrast, from solutions of the analogous BF_4^- complexes **7**, **10** and **16** in the less polar solvent MeCN only dinuclear species are isolated.

Given that our primary interest in pldpt (**3**) was to use it to prepare and study further examples of, prior to our re-

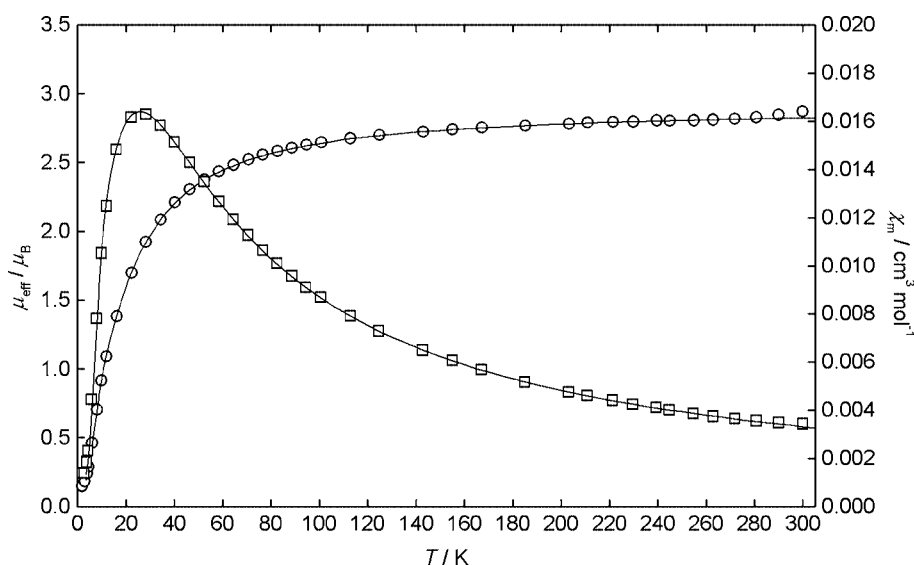


Figure 8. Temperature dependence of the effective magnetic moment μ_{eff} (○) and the molar magnetic susceptibility χ_m (□) per nickel(II) centre for $\text{Ni}^{\text{II}}_2(\text{pldpt})_2(\text{ClO}_4)_4(\text{MeCN})_m(\text{H}_2\text{O})_n$ (**9**) ($m = 0$, $n = 0$). The solid lines represent the best fit using the parameters given in Table 5.

search, rarely observed, discrete dinuclear complexes of 4-substituted-3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles, the deliberate preparation of mononuclear complexes employing metal-to-ligand molar ratios of 1:2 or 1:3 was not attempted in the course of this particular study. However, such studies are currently being carried out as an integral component of our ongoing investigation into the iron(II) coordination chemistry of pldpt (**3**) and related ligands.^[52]

The enhanced dinucleating ability of pldpt (**3**), as compared to the 4-aryl-3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles, is attributed largely to the effect of the 4-(1*H*-pyrrol-1-yl) group on the relative solubility of the various possible products in the solvents employed. The X-ray crystallographic data, and the NMR spectroscopic data for the zinc(II) complex **15**, indicate that the electronic effect of this particular substituent is probably quite small because the potentially strong π -donation from the pyrrole ring is switched off due to the near-perpendicular orientation of the pyrrole ring relative to the triazole ring, leaving only the effects transmitted by the σ -pathway, which are likely to be weak. These findings are consistent with the suggestion that the substituent on *N*⁴ in 4-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles influences the ability of such a ligand to form only mononuclear or both di- and mononuclear complexes by a complex mixture of factors, the most important of which, in the case of pldpt (**3**), appears to be its effect on the relative solubility of the various possible products in the solvents employed during the preparation and/or the recrystallisation of the complexes, although in other cases subtle electronic effects may also be at work.^[2,31,32,52]

Magnetic studies carried out on the dinuclear cobalt(II) complexes **4** and **7** and the dinuclear nickel(II) complexes **9** and **10** have shown that the two central triazole bridges provided by pldpt (**3**) mediate weak antiferromagnetic exchange coupling between the two metal centres of these complexes. With a view to systematically accessing families of spin crossover systems, the exploration of the coordination behaviour of pldpt (**3**), and related ligands, towards iron(II) salts in 1:1, 1:2 and 1:3 metal-to-ligand molar ratios, in a variety of solvents, is well underway and the results of this study will be reported in due course.^[52]

Experimental Section

General Remarks: All solvents used for reactions were laboratory reagent grade while UV/Vis/NIR and conductivity measurements were carried out in HPLC-grade solvents. All chemicals were purchased from Aldrich and used as received. Elemental analyses were carried out by the Campbell Microanalytical Laboratory at the University of Otago. Melting points were determined with a Galenkamp melting point apparatus in open-glass capillaries and are uncorrected. ¹H and ¹³C NMR spectra were recorded with a Varian INOVA-500 spectrometer at 25 °C. Chemical shifts are given relative to TMS using the residual solvent signals as secondary reference (CDCl₃: δ_{H} = 7.26 ppm, δ_{C} = 77.16 ppm; [D₇]DMF: δ_{H} = 8.02 ppm, δ_{C} = 163.15 ppm). Peak assignments were made on the basis of chemical shifts, integration patterns and coupling constants as well as two-dimensional correlation experiments where necessary. IR spectra were recorded in the range 4000–400 cm^{−1}

with a Perkin–Elmer Spectrum BX FT-IR spectrophotometer. UV/Vis/NIR spectra were recorded with a Varian CARY 500 Scan UV/Vis/NIR spectrophotometer in the range 200–1400 nm. Conductivity measurements were carried out at 25 °C using a Suntext SC-170 conductivity meter. ESI mass spectra of organic compounds were run on a Shimadzu LCMS-QP8000a spectrometer while spectra of complexes were run on a MicroMass LCT spectrometer. For all compounds MeCN was used as the solvent. Magnetic data were recorded in the range 300–4.2 K using a Quantum Design MPMS5 SQUID magnetometer with an applied field of 1 T.

Caution: While no problems were encountered in the course of this work, reactions involving N₂H₄·H₂O may form potentially explosive mixtures so must be carried out with extreme caution. Similarly, ClO₄[−] salts are potentially explosive so should be handled with appropriate care.

3,6-Di(2-pyridyl)-1,4-dihydro-1,2,4,5-tetrazine (1): A heterogeneous mixture of 2-pyridinecarbonitrile (20.8 g, 0.20 mol) and N₂H₄·H₂O (50 mL) was refluxed for 2 hours during which time the mixture became homogeneous, turned orange and a solid separated from the solution with heavy foaming. After cooling, all volatiles were evaporated under reduced pressure and the orange solid thus obtained was dried in vacuo. Recrystallisation from pyridine gave 13.8 g (58%) of analytically pure 3,6-di(2-pyridyl)-1,4-dihydro-1,2,4,5-tetrazine (**1**) as bright orange needles. M.p. 191–193 °C. C₁₂H₁₀N₆ (238.25): calcd. C 60.50, H 4.23, N 35.27; found C 60.50, H 4.14, N 35.33. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 7.34 [ddd, ³*J*_{4,5} = 7.7 Hz, ³*J*_{5,6} = 4.8 Hz, ⁴*J*_{3,5} = 1.2 Hz, 2 H, 2 × 5-PyH], 7.74 [dt, ³*J*_{3,4} = ³*J*_{4,5} = 7.7 Hz, ⁴*J*_{4,6} = 1.8 Hz, 2 H, 2 × 4-PyH], 8.05 [ddd, ³*J*_{3,4} = 7.7 Hz, ⁴*J*_{3,5} = 1.2 Hz, ⁵*J*_{3,6} = 0.9 Hz, 2 H, 2 × 3-PyH], 8.54–8.59 [m, 4 H, 2 × 6-PyH and 2 × PyCNH]. ¹³C{¹H} NMR (125 MHz, CDCl₃, ppm): δ = 121.41 [2 × 3-PyC], 124.97 [2 × 5-PyC], 136.83 [2 × 4-PyC], 146.75 [2 × NCNH], 147.65 [2 × 2-PyC], 148.51 [2 × 6-PyC]. IR (KBr): $\tilde{\nu}$ = 3343, 3296, 3058, 1588, 1564, 1470, 1446, 1387, 1288, 1251, 1155, 1117, 1089, 1077, 1041, 995, 981, 903, 885, 795, 787, 771, 745, 720, 677, 667, 655, 622, 490 cm^{−1}. ESI-MS (pos., MeCN): *m/z* = 239 [M + H]⁺, 261 [M + Na]⁺, 277 [M + K]⁺.

4-Amino-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole (NH₂dpt, 2): 3,6-Di(2-pyridyl)-1,4-dihydro-1,2,4,5-tetrazine (**1**) (11.9 g, 50.0 mmol) was dissolved in 2 M HCl (100 mL) and the dark brown solution was refluxed for 30 minutes. After cooling, the resulting golden solution was basified to pH ≈ 9 by dropwise addition of concd. NH₃ resulting in the formation of a voluminous colourless precipitate. The solid was filtered off, washed with H₂O and dried in vacuo. Recrystallisation from H₂O/EtOH (1:1) gave 10.1 g (84%) of analytically pure NH₂dpt (**2**) as colourless needles. Alternatively, a mixture of 2-pyridinecarbonitrile (10.4 g, 0.10 mol), N₂H₄·H₂SO₄ (13.0 g, 0.10 mol) and N₂H₄·H₂O (15.0 g, 0.30 mol) in 1,2-ethanediol (50 mL) was heated at 130 °C for 24 hours. An orange solid that soon separated from the solution with heavy foaming redissolved almost completely over time. On cooling to room temperature, the reaction mixture solidified to give an almost colourless solid contaminated with some orange material. H₂O (100 mL) was added, the resulting slurry was filtered and the crude product was washed with water and dried in vacuo. Recrystallisation from H₂O/EtOH (1:1) gave 8.06 g (67%) of crude NH₂dpt (**2**) as a yellowish solid. This material could be used in the next step without further purification. Analytically pure material was obtained as colourless needles only after at least one more recrystallisation from H₂O/EtOH (1:1). M.p. 185–187 °C. C₁₂H₁₀N₆ (238.25): calcd. C 60.50, H 4.23, N 35.27; found C 60.35, H 4.10, N 35.00. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 7.36 [ddd, ³*J*_{4,5} = 7.7 Hz, ³*J*_{5,6} =

4.8 Hz, $^4J_{3,5} = 1.2$ Hz, 2 H, 2 $\times$ 5-PyH], 7.86 [dt, $^3J_{3,4} = ^3J_{4,5} = 7.7$ Hz, $^4J_{4,6} = 1.8$ Hz, 2 H, 2 $\times$ 4-PyH], 8.38 [ddd, $^3J_{3,4} = 7.7$ Hz, $^4J_{3,5} = 1.2$ Hz, $^5J_{3,6} = 0.9$ Hz, 2 H, 2 $\times$ 3-PyH], 8.49 [br. s, 2 H, TzNH₂], 8.65 [ddd, $^3J_{5,6} = 4.8$ Hz, $^4J_{4,6} = 1.8$ Hz, $^5J_{3,6} = 0.9$ Hz, 2 H, 2 $\times$ 6-PyH]. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl₃, ppm): $\delta = 122.97$ [2 $\times$ 3-PyC], 124.11 [2 $\times$ 5-PyC], 137.41 [2 $\times$ 4-PyC], 147.82 [3- and 5-TzC], 148.10 [2 $\times$ 2-PyC], 148.43 [2 $\times$ 6-PyC]. IR (KBr): $\tilde{\nu} = 3421$, 3293, 1588, 1566, 1545, 1465, 1432, 1412, 1390, 1318, 1273, 1249, 1148, 1093, 1074, 1041, 998, 968, 912, 795, 787, 737, 693, 677, 623, 586, 489 cm⁻¹. ESI-MS (pos., MeCN): $m/z = 239$ [M + H]⁺, 261 [M + Na]⁺, 277 [M + K]⁺.

3,5-Di(2-pyridyl)-4-(1H-pyrrol-1-yl)-4H-1,2,4-triazole (pldpt, 3): A mixture of NH₂dpt (2) (4.77 g, 20 mmol) and 2,5-dimethoxytetrahydrofuran (3.30 g, 25.0 mmol) in 1,4-dioxane (20 mL) and acetic acid (20 mL) was refluxed for 24 hours. After cooling, all volatiles were removed in vacuo to give a dark crystalline solid. This was taken up in CH₂Cl₂ (50 mL) and the mixture was filtered through a short column of silica gel. The filtrate was evaporated under reduced pressure and the yellowish solid thus obtained was dried in vacuo. Recrystallisation from EtOH gave 4.46 g (77%) of analytically pure pldpt (3) as colourless needles. M.p. 199–201 °C. C₁₆H₁₂N₆ (288.31): calcd. C 66.66, H 4.20, N 29.15; found C 66.90, H 3.96, N 29.22. ^1H NMR (500 MHz, CDCl₃, ppm): $\delta = 6.22$ [t, $^3J = 2.4$ Hz, 2 H, 3- and 4-PIH], 6.86 [t, $^3J = 2.4$ Hz, 2 H, 2- and 5-PIH], 7.30 [ddd, $^3J_{4,5} = 7.7$ Hz, $^3J_{5,6} = 4.8$ Hz, $^4J_{3,5} = 1.2$ Hz, 2 H, 2 $\times$ 5-PyH], 7.75 [dt, $^3J_{3,4} = ^3J_{4,5} = 7.7$ Hz, $^4J_{4,6} = 1.8$ Hz, 2 H, 2 $\times$ 4-PyH], 7.84 [ddd, $^3J_{3,4} = 7.7$ Hz, $^4J_{3,5} = 1.2$ Hz, $^5J_{3,6} = 0.9$ Hz, 2 H, 2 $\times$ 3-PyH], 8.52 [ddd, $^3J_{5,6} = 4.8$ Hz, $^4J_{4,6} = 1.8$ Hz, $^5J_{3,6} = 0.9$ Hz, 2 H, 2 $\times$ 6-PyH]. ^1H NMR (500 MHz, [D₇]DMF, ppm): $\delta = 6.12$ [t, $^3J = 2.4$ Hz, 2 H, 3- and 4-PIH], 7.20 [t, $^3J = 2.4$ Hz, 2 H, 2- and 5-PIH], 7.51 [ddd, $^3J_{4,5} = 7.7$ Hz, $^3J_{5,6} = 4.8$ Hz, $^4J_{3,5} = 1.2$ Hz, 2 H, 2 $\times$ 5-PyH], 7.95 [ddd, $^3J_{3,4} = 7.7$ Hz, $^4J_{3,5} = 1.2$ Hz, $^5J_{3,6} = 0.9$ Hz, 2 H, 2 $\times$ 3-PyH], 8.00 [dt, $^3J_{3,4} = ^3J_{4,5} = 7.7$ Hz, $^4J_{4,6} = 1.8$ Hz, 2 H, 2 $\times$ 4-PyH], 8.54 [ddd, $^3J_{5,6} = 4.8$ Hz, $^4J_{4,6} = 1.8$ Hz, $^5J_{3,6} = 0.9$ Hz, 2 H, 2 $\times$ 6-PyH]. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl₃, ppm): $\delta = 108.44$ [3- and 4-PIC], 122.34 [2- and 5-PIC], 123.54 [2 $\times$ 3-PyC], 124.90 [2 $\times$ 5-PyC], 136.84 [2 $\times$ 4-PyC], 145.33 [2 $\times$ 2-PyC], 149.93 [2 $\times$ 6-PyC], 153.16 [3- and 5-TzC]. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, [D₇]DMF, ppm): $\delta = 108.51$ [3- and 4-PIC], 124.02 [2- and 5-PIC], 124.74 [2 $\times$ 3-PyC], 126.16 [2 $\times$ 5-PyC], 138.21 [2 $\times$ 4-PyC], 146.69 [2 $\times$ 2-PyC], 150.79 [2 $\times$ 6-PyC], 154.15 [3- and 5-TzC]. IR (KBr): $\tilde{\nu} = 3118$, 1587, 1569, 1533, 1465, 1443, 1435, 1423, 1332, 1281, 1246, 1181, 1150, 1088, 1069, 1044, 1010, 992, 963, 912, 790, 736, 729, 710, 703, 633, 619, 608, 524, 489 cm⁻¹. ESI-MS (pos., MeCN): $m/z = 289$ [M + H]⁺, 311 [M + Na]⁺, 327 [M + K]⁺. UV/Vis/NIR (MeCN): λ_{max} ($\epsilon/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) = 251 (14600), 281 nm (18500).

Reaction of pldpt (3) with CoCl₂·6H₂O (Method A): A pinkish-red solution of CoCl₂·6H₂O (238 mg, 1.00 mmol) in H₂O (5 mL) was added to a colourless solution of pldpt (3) (288 mg, 1.00 mmol) in MeOH (20 mL) dropwise at room temperature and the resulting orange-brown solution was stirred for 30 minutes. Slow evaporation over the course of 4 weeks led to the formation of a large quantity of a beige solid and a few tiny orange prisms. The solid products were filtered off and washed with MeOH. Drying in vacuo gave Co^{II}(pldpt)₂Cl₂(H₂O)_{1.5}. C₃₂H₂₇Cl₂CoN₁₂O_{1.5} (733.49): calcd. C 52.40, H 3.71, N 22.92, Cl 9.67; found C 52.36, H 3.49, N 23.17, Cl 9.66.

Reaction of pldpt (3) with CoCl₂·6H₂O (Method B): A deep blue solution of CoCl₂·6H₂O (238 mg, 1.00 mmol) in EtOH (5 mL) was added to a colourless refluxing solution of pldpt (3) (288 mg, 1.00 mmol) in EtOH (20 mL). A blue solid formed almost immedi-

ately. The resulting suspension was refluxed for another 15 minutes and was then stirred at room temperature for 24 hours. The solid was filtered off and washed with EtOH. Drying in vacuo gave 388 mg (ca. 90%) of Co^{II}₂(pldpt)₂Cl₄(H₂O) as a pink powder. C₃₂H₂₆Cl₄Co₂N₁₂O (854.32): calcd. C 44.99, H 3.07, N 19.67; found C 45.38, H 3.05, N 19.51.

Reaction of pldpt (3) with Co(ClO₄)₂·6H₂O: An orange solution of Co(ClO₄)₂·6H₂O (366 mg, 1.00 mmol) in MeCN (5 mL) was added to a colourless refluxing solution of pldpt (3) (288 mg, 1.00 mmol) in MeCN (20 mL). An orange solid formed almost immediately. The resulting suspension was cooled to room temperature and the solid was filtered off and washed with MeCN. Drying in vacuo gave 555 mg (ca. 90%) of Co^{II}₂(pldpt)₂(ClO₄)₄(MeCN)_{*m*}(H₂O)_{*n*} (4) as a pale orange powder. The solvent content of the initial products varied considerably from batch to batch. Heating of the powders at 60 °C in vacuo for several days similarly afforded materials of variable solvent content. A sample analysing as Co^{II}₂(pldpt)₂(ClO₄)₄(MeCN) was used for characterisation purposes. C₃₄H₂₇Cl₄Co₂N₁₃O₁₆ (1133.34): calcd. C 36.03, H 2.40, N 16.07; found C 36.08, H 2.54, N 16.26. IR (KBr): $\tilde{\nu} = 1611$, 1544, 1517, 1473, 1439, 1405, 1354, 1302, 1263, 1188, 1113, 1074, 1012, 931, 911, 794, 746, 725, 701, 654, 635, 625 cm⁻¹. ESI-MS (pos., MeCN): $m/z = 235.1$ [Co(pldpt)(MeCN)₃]²⁺, 289.1 [(pldpt)H]⁺, 338.1 [Co(pldpt)₂(MeCN)]²⁺, 446.0 [Co(pldpt)(ClO₄)]⁺, 461.7 [Co(pldpt)₃]²⁺, 487.0 [Co(pldpt)(MeCN)(ClO₄)]⁺, 577.4 [(pldpt)₂-H]⁺, 734.3 [Co(pldpt)₂(ClO₄)]⁺, 993.3 [Co₂(pldpt)₂(ClO₄)₃]⁺. Molar conductivity (DMF): $\Lambda_m = 260 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$. Vapour diffusion of Et₂O into an orange solution of complex 4 in MeCN/DMF (10:1) afforded orange crystals of [Co^{II}₂(pldpt)₂(H₂O)₂(DMF)₂](ClO₄)₄·0.5Et₂O (5) and yellow crystals of [Co^{II}(pldpt)₂(DMF)₂](ClO₄)₂ (6).

Reaction of pldpt (3) with Co(BF₄)₂·6H₂O: An orange solution of Co(BF₄)₂·6H₂O (341 mg, 1.00 mmol) in MeCN (5 mL) was added to a colourless refluxing solution of pldpt (3) (288 mg, 1.00 mmol) in MeCN (20 mL). The resulting orange solution was refluxed for 10 minutes and was then stirred at room temperature for another 4 hours during which time an orange precipitate formed. The solid was filtered off and washed with MeCN. Drying in vacuo gave 465 mg (ca. 80%) of Co^{II}₂(pldpt)₂(BF₄)₄(MeCN)_{*m*}(H₂O)_{*n*} (7) as a pale orange powder. The solvent content of the initial products varied considerably from batch to batch. Heating of the powders at 60 °C in vacuo for several days similarly afforded materials of variable solvent content. A sample analysing as Co^{II}₂(pldpt)₂(BF₄)₄(MeCN)(H₂O)₂ was used for characterisation purposes. C₃₄H₃₁B₄Co₂F₁₆N₁₃O₂ (1118.79): calcd. C 36.50, H 2.79, N 16.28; found C 36.37, H 2.75, N 16.17. IR (KBr): $\tilde{\nu} = 1610$, 1577, 1545, 1518, 1474, 1440, 1402, 1356, 1297, 1263, 1189, 1073, 911, 862, 796, 765, 749, 727, 705, 655, 636, 563, 533, 521, 436, 414 cm⁻¹. ESI-MS (pos., MeCN): $m/z = 289.1$ [(pldpt)H]⁺, 317.6 [Co(pldpt)₂]²⁺, 338.1 [Co(pldpt)₂(MeCN)]²⁺, 461.7 [Co(pldpt)₃]²⁺, 722.3 [Co(pldpt)₂(BF₄)]⁺. UV/Vis/NIR (MeCN): λ_{max} ($\epsilon/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) = 252 (25200), 291 (37000), 481 (46), 1022 nm (12). Molar conductivity (MeCN): $\Lambda_m = 480 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$. Molar conductivity (DMF): $\Lambda_m = 280 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$. Vapour diffusion of Et₂O into the orange MeCN mother liquor or an orange solution of complex 7 in MeCN afforded orange crystals of [Co^{II}₂(pldpt)₂(MeCN)₂(H₂O)₂](BF₄)₄ (8).

Reaction of pldpt (3) with NiCl₂·6H₂O (Method A): A grass green solution of NiCl₂·6H₂O (238 mg, 1.00 mmol) in H₂O (5 mL) was added to a colourless solution of pldpt (3) (288 mg, 1.00 mmol) in MeOH (20 mL) dropwise at room temperature and the resulting olive-green solution was stirred for 30 minutes. Slow evaporation over the course of 6 weeks led to the formation of an inseparable

mixture of a greenish crystalline solid and blue prisms in an estimated 3:1 ratio. These were not easily separable so no analytical data were obtained for either of the products.

Reaction of pldpt (3) with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Method B): A grass green solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (238 mg, 1.00 mmol) in EtOH (5 mL) was added to a colourless solution of pldpt (3) (288 mg, 1.00 mmol) in EtOH (20 mL) dropwise at room temperature. The resulting green solution was stirred at room temperature for 4 hours during which time a green precipitate formed. The solid was filtered off and washed with EtOH. Drying in vacuo gave 275 mg (ca. 60%) of $\text{Ni}^{\text{II}}_2(\text{pldpt})_2\text{Cl}_4(\text{H}_2\text{O})_3$ as a very pale green powder. $\text{C}_{32}\text{H}_{30}\text{Cl}_4\text{Ni}_2\text{N}_{12}\text{O}_3$ (889.86): calcd. C 43.19, H 3.40, N 18.89; found C 43.62, H 3.28, N 18.74.

Reaction of pldpt (3) with $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$: A blue solution of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (366 mg, 1.00 mmol) in MeCN (5 mL) was added to a colourless refluxing solution of pldpt (3) (288 mg, 1.00 mmol) in MeCN (20 mL). A purple solid formed almost immediately. The resulting suspension was cooled to room temperature and the solid was filtered off and washed with MeCN. Drying in vacuo gave 475 mg (ca. 80%) of $\text{Ni}^{\text{II}}_2(\text{pldpt})_2(\text{ClO}_4)_4(\text{MeCN})_m(\text{H}_2\text{O})_n$ (9) as a pale violet powder. The solvent content of the initial products varied considerably from batch to batch. Heating of the powders at 60 °C in vacuo for several days similarly afforded materials of variable solvent content. A sample analysing as $\text{Ni}^{\text{II}}_2(\text{pldpt})_2(\text{ClO}_4)_4$ was used for characterisation purposes. $\text{C}_{32}\text{H}_{24}\text{Cl}_4\text{Ni}_2\text{N}_{12}\text{O}_{16}$ (1091.81): calcd. C 35.20, H 2.22, N 15.39; found C 35.18, H 2.53, N 15.59. IR (KBr): $\tilde{\nu}$ = 1612, 1548, 1526, 1517, 1474, 1440, 1410, 1355, 1304, 1265, 1195, 1114, 1074, 1025, 1012, 931, 911, 793, 747, 725, 700, 659, 636, 625 cm^{-1} . ESI-MS (pos., MeCN): m/z = 214.1 $[\text{Ni}(\text{pldpt})(\text{MeCN})_2]^{2+}$, 234.6 $[\text{Ni}(\text{pldpt})(\text{MeCN})_3]^{2+}$, 255.1 $[\text{Ni}(\text{pldpt})(\text{MeCN})_4]^{2+}$, 289.1 $[(\text{pldpt})\text{H}]^+$, 317.1 $[\text{Ni}(\text{pldpt})_2]^{2+}$, 337.7 $[\text{Ni}(\text{pldpt})_2(\text{MeCN})]^{2+}$, 358.2 $[\text{Ni}(\text{pldpt})_2(\text{MeCN})_2]^{2+}$, 445.0 $[\text{Ni}(\text{pldpt})(\text{ClO}_4)]^+$, 461.1 $[\text{Ni}(\text{pldpt})_3]^{2+}$, 486.0 $[\text{Ni}(\text{pldpt})(\text{MeCN})(\text{ClO}_4)]^+$, 527.1 $[\text{Ni}(\text{pldpt})(\text{MeCN})_2(\text{ClO}_4)]^+$, 568.2 $[\text{Ni}(\text{pldpt})(\text{MeCN})_3(\text{ClO}_4)]^+$, 577.4 $[(\text{pldpt})_2\text{H}]^+$, 733.2 $[\text{Ni}(\text{pldpt})_2(\text{ClO}_4)]^+$, 991.2 $[\text{Ni}_2(\text{pldpt})_2(\text{ClO}_4)_3]^+$. Molar conductivity (DMF): Λ_m = 300 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$.

Reaction of pldpt (3) with $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$: A blue solution of $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (340 mg, 1.00 mmol) in MeCN (5 mL) was added to a colourless refluxing solution of pldpt (3) (288 mg, 1.00 mmol) in MeCN (20 mL). The resulting purple solution was refluxed for 10 minutes and was then stirred at room temperature for another 4 hours during which time a purple precipitate formed. The solid was filtered off and washed with MeCN. Drying in vacuo gave 215 mg (ca. 40%) of $\text{Ni}^{\text{II}}_2(\text{pldpt})_2(\text{BF}_4)_4(\text{MeCN})_m(\text{H}_2\text{O})_n$ (10) as a pale violet powder. The solvent content of the initial products varied considerably from batch to batch. Heating of the powders at 60 °C in vacuo for several days similarly afforded materials of variable solvent content. A sample analysing as $\text{Ni}^{\text{II}}_2(\text{pldpt})_2(\text{BF}_4)_4(\text{H}_2\text{O})_4$ was used for characterisation purposes. $\text{C}_{32}\text{H}_{32}\text{B}_4\text{F}_{16}\text{Ni}_2\text{N}_{12}\text{O}_4$ (1113.28): calcd. C 34.52, H 2.90, N 15.10; found C 34.55, H 2.70, N 15.09. IR (KBr): $\tilde{\nu}$ = 1612, 1578, 1549, 1521, 1475, 1441, 1410, 1356, 1300, 1265, 1190, 1073, 911, 796, 750, 727, 705, 694, 659, 637, 564, 533, 522, 439, 415 cm^{-1} . ESI-MS (pos., MeCN): m/z = 289.1 $[(\text{pldpt})\text{H}]^+$, 317.1 $[\text{Ni}(\text{pldpt})_2]^{2+}$, 337.6 $[\text{Ni}(\text{pldpt})_2(\text{MeCN})]^{2+}$, 358.1 $[\text{Ni}(\text{pldpt})_2(\text{MeCN})_2]^{2+}$, 461.1 $[\text{Ni}(\text{pldpt})_3]^{2+}$, 721.3 $[\text{Ni}(\text{pldpt})_2(\text{BF}_4)]^+$. UV/Vis/NIR (MeCN): λ_{max} ($\epsilon/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) = 238 (24400), 295 (36400), ca. 530 sh (ca. 70), 866 nm (40). Molar conductivity (MeCN): Λ_m = 470 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Molar conductivity (DMF): Λ_m = 250 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Vapour diffusion of Et₂O into the purple MeCN mother liquor or a purple solution of complex 10 in MeCN

afforded purple crystals of $[\text{Ni}^{\text{II}}_2(\text{pldpt})_2(\text{MeCN})_4](\text{BF}_4)_4 \cdot 2\text{MeCN}$ (11).

Reaction of pldpt (3) with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$: A blue solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (371 mg, 1.00 mmol) in MeCN (5 mL) was added to a colourless refluxing solution of pldpt (3) (288 mg, 1.00 mmol) in MeCN (20 mL). The resulting green solution was refluxed for 10 minutes and was then stirred at room temperature for another 4 hours during which time a blue precipitate formed. The solid was filtered off and washed with a minimum amount of MeCN. Drying in vacuo gave 249 mg (59%) of $[\text{Cu}^{\text{II}}(\text{pldpt})_2(\text{ClO}_4)_2]$ (12) as a blue powder. $\text{C}_{32}\text{H}_{24}\text{Cl}_2\text{CuN}_{12}\text{O}_8$ (839.07): calcd. C 45.81, H 2.88, N 20.03; found C 45.52, H 2.78, N 20.05. IR (KBr): $\tilde{\nu}$ = 1614, 1588, 1571, 1554, 1533, 1513, 1485, 1456, 1434, 1340, 1311, 1272, 1193, 1105, 1023, 991, 929, 913, 793, 750, 742, 722, 698, 645, 622, 568, 495 cm^{-1} . ESI-MS (pos., MeCN): m/z = 289.1 $[(\text{pldpt})\text{H}]^+$, 319.6 $[\text{Cu}(\text{pldpt})_2]^{2+}$, 340.1 $[\text{Cu}(\text{pldpt})_2(\text{MeCN})]^{2+}$, 351.0 $[\text{Cu}(\text{pldpt})]^{2+}$, 369.1 $[\text{Cu}(\text{pldpt})(\text{H}_2\text{O})]^+$, 392.1 $[\text{Cu}(\text{pldpt})(\text{MeCN})]^+$, 639.2 $[\text{Cu}(\text{pldpt})_2]^+$, 738.2 $[\text{Cu}(\text{pldpt})_2(\text{ClO}_4)]^+$. UV/Vis/NIR (MeCN): λ_{max} ($\epsilon/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) = 242 (35000), 295 (33500), 659 nm (90). Molar conductivity (MeCN): Λ_m = 245 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Vapour diffusion of Et₂O into a blue solution of complex 12 in MeCN gave blue crystals of $[\text{Cu}^{\text{II}}(\text{pldpt})_2(\text{ClO}_4)_2] \cdot 2\text{DMF}$ (13) while vapour diffusion of Et₂O into the green MeCN mother liquor afforded green crystals of $[\text{Cu}^{\text{II}}_2(\text{pldpt})_2(\text{H}_2\text{O})_2(\text{MeCN})_2](\text{ClO}_4)_4$ (14). The occurrence of the DMF solvates in complex 13 was probably due to the use of contaminated glassware.

Reaction of pldpt (3) with $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$: A colourless solution of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (372 mg, 1.00 mmol) in MeCN (5 mL) was added to a colourless refluxing solution of pldpt (3) (288 mg, 1.00 mmol) in MeCN (20 mL). A colourless solid formed almost immediately. The resulting suspension was cooled to room temperature and the solid was filtered off and washed with MeCN. Drying in vacuo gave 470 mg (ca. 80%) of $\text{Zn}^{\text{II}}_2(\text{pldpt})_2(\text{ClO}_4)_4(\text{MeCN})_m(\text{H}_2\text{O})_n$ (15) as a colourless powder. The solvent content of the initial products varied considerably from batch to batch. Heating of the powders at 60 °C in vacuo for several days similarly afforded materials of variable solvent content. A sample analysing as $\text{Zn}^{\text{II}}_2(\text{pldpt})_2(\text{ClO}_4)_4(\text{H}_2\text{O})_4$ was used for characterisation purposes. $\text{C}_{32}\text{H}_{32}\text{Cl}_4\text{N}_{12}\text{O}_{20}\text{Zn}_2$ (1177.25): calcd. C 32.65, H 2.74, N 14.28; found C 32.28, H 2.59, N 14.30. ¹H NMR (500 MHz, [D₇]-DMF, ppm): δ = 6.35 [t, ³J = 2.4 Hz, 4 H, 2 × 3- and 4-PIH], 7.37 [t, ³J = 2.4 Hz, 4 H, 2 × 2- and 5-PIH], 7.55 [br. s, 4 H, 4 × 3-PyH], 7.69 [ddd, ³J_{4,5} = 7.7 Hz, ³J_{5,6} = 4.8 Hz, ⁴J_{3,5} = 1.2 Hz, 4 H, 4 × 5-PyH], 8.12 [dt, ³J_{3,4} = ³J_{4,5} = 7.7 Hz, ⁴J_{4,6} = 1.8 Hz, 4 H, 4 × 4-PyH], 8.68 [ddd, ³J_{5,6} = 4.8 Hz, ⁴J_{4,6} = 1.8 Hz, ⁵J_{3,6} = 0.9 Hz, 4 H, 4 × 6-PyH]. ¹³C{¹H} NMR (125 MHz, [D₇]-DMF, ppm): δ = 109.91 [2 × 3- and 4-PI-C], 123.38 [2 × 2- and 5-PI-C], 124.08 [4 × 3-Py-C], 127.49 [4 × 5-Py-C], 139.61 [4 × 4-Py-C], 144.25 [4 × 2-Py-C], 150.95 [4 × 6-Py-C], 154.01 [2 × 3- and 5-Tz-C]. IR (KBr): $\tilde{\nu}$ = 1611, 1546, 1525, 1517, 1476, 1441, 1354, 1306, 1297, 1264, 1192, 1117, 1089, 1014, 930, 911, 795, 748, 724, 703, 653, 636, 625 cm^{-1} . ESI-MS (pos., MeCN): m/z = 217.1 $[\text{Zn}(\text{pldpt})(\text{MeCN})_2]^{2+}$, 237.6 $[\text{Zn}(\text{pldpt})(\text{MeCN})_3]^{2+}$, 289.1 $[(\text{pldpt})\text{H}]^+$, 320.1 $[\text{Zn}(\text{pldpt})_2]^{2+}$, 340.7 $[\text{Zn}(\text{pldpt})_2(\text{MeCN})]^{2+}$, 451.1 $[\text{Zn}(\text{pldpt})(\text{ClO}_4)]^+$, 464.3 $[\text{Zn}(\text{pldpt})_3]^{2+}$, 492.2 $[\text{Zn}(\text{pldpt})(\text{MeCN})(\text{ClO}_4)]^+$, 577.4 $[(\text{pldpt})_2\text{H}]^+$, 739.3 $[\text{Zn}(\text{pldpt})_2(\text{ClO}_4)]^+$, 1003.1 $[\text{Zn}_2(\text{pldpt})_2(\text{ClO}_4)_3]^+$. Molar conductivity (DMF): Λ_m = 255 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$.

Reaction of pldpt (3) with $\text{Zn}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$: A colourless solution of $\text{Zn}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (347 mg, 1.00 mmol) in MeCN (5 mL) was added to a colourless refluxing solution of pldpt (3) (288 mg, 1.00 mmol) in MeCN (20 mL). The resulting colourless solution was refluxed for 10 minutes and was then stirred at room temperature for an

Table 6. Crystallographic data for 3,5-di(2-pyridyl)-4-(1*H*-pyrrol-1-yl)-4*H*-1,2,4-triazole (pldpt, **3**), [Co^{II}₂(pldpt)₂(DMF)₂(H₂O)₂](ClO₄)₄·0.5Et₂O (**5**), [Co^{II}(pldpt)₂(DMF)₂](ClO₄)₂ (**6**), [Co^{II}₂(pldpt)₂(MeCN)₂(H₂O)₂](BF₄)₄ (**8**), [Ni^{II}₂(pldpt)₂(MeCN)₄](BF₄)₄·2MeCN (**11**), [Cu^{II}(pldpt)₂(ClO₄)₂·2DMF (**13**), [Cu^{II}₂(pldpt)₂(MeCN)₂(H₂O)₂](ClO₄)₄ (**14**) and [Zn^{II}₂(pldpt)₂(MeCN)₂(H₂O)₂](BF₄)₄ (**17**).

	3	5	6	8
Empirical formula	C ₁₆ H ₁₂ N ₆	C ₄₀ H ₄₇ Cl ₄ Co ₂ N ₁₄ O _{20.5}	C ₃₈ H ₃₈ Cl ₂ CoN ₁₄ O ₁₀	C ₃₆ H ₃₄ B ₄ Co ₂ F ₁₆ N ₁₄ O ₂
Formula weight [g mol ⁻¹]	288.32	1311.58	980.65	1159.87
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	<i>P</i> 2 ₁	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> [Å]	10.0461(2)	10.349(2)	8.8443(1)	9.9087(3)
<i>b</i> [Å]	7.3951(2)	12.680(3)	13.3043(2)	10.3844(4)
<i>c</i> [Å]	19.1277(5)	13.065(3)	11.2462(2)	11.8599(4)
<i>a</i> [°]	90	76.62(3)	90	76.834(1)
<i>β</i> [°]	103.000(1)	88.30(3)	82.518(1)	74.254(1)
<i>γ</i> [°]	90	72.46(3)	90	85.140(1)
<i>V</i> [Å ³]	1384.61(6)	1588.9(5)	2128.70(5)	1143.33(7)
<i>Z</i>	4	1	2	1
<i>ρ</i> _{calcd.} [g cm ⁻³]	1.383	1.371	1.530	1.685
<i>μ</i> [mm ⁻¹]	0.089	0.765	0.604	0.844
Temperature [K]	83(2)	200(2)	200(2)	83(2)
<i>F</i> (000)	600	671	1010	582
Crystal colour and shape	colourless block	orange prism	yellow block	orange prism
Crystal size [mm ³]	0.50 × 0.50 × 0.36	0.34 × 0.32 × 0.30	0.36 × 0.12 × 0.10	0.40 × 0.22 × 0.18
<i>θ</i> _{min.} / <i>θ</i> _{max.} [°]	2.08/25.63	1.60/26.45	1.90/31.07	1.83/27.13
<i>h</i>	−12 → 12	−12 → 12	−11 → 11	−12 → 12
<i>k</i>	−7 → 9	−15 → 15	−17 → 17	−12 → 13
<i>l</i>	−21 → 23	−16 → 16	−23 → 23	0 → 15
Reflections collected	7900	11447	20754	11760
Independent reflections	4140 [<i>R</i> (int) = 0.0109]	6364 [<i>R</i> (int) = 0.0741]	4677 [<i>R</i> (int) = 0.0632]	4996 [<i>R</i> (int) = 0.0156]
Completeness to <i>θ</i> _{max.} [%]	99.6	97.3	68.5	98.6
Data/restraints/parameter	4140/1/397	6364/10/421	4677/0/295	4996/0/343
GOF	1.055	1.023	1.067	1.026
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0242/0.0610	0.0902/0.2579	0.0677/0.1622	0.0245/0.0597
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0249/0.0613	0.1204/0.2926	0.1035/0.1818	0.0286/0.0618
Absolute structure factor	−0.2(11)			
Max. peak/hole [e·Å ⁻³]	0.156/−0.189	1.316/−1.049	0.511/−0.712	0.349/−0.357
	11	13	14	17
Empirical formula	C ₄₄ H ₄₂ B ₄ F ₁₆ N ₁₈ Ni ₂	C ₃₈ H ₃₈ Cl ₂ CuN ₁₄ O ₁₀	C ₃₆ H ₃₄ Cl ₄ Cu ₂ N ₁₄ O ₁₈	C ₃₆ H ₃₄ B ₄ F ₁₆ N ₁₄ O ₂ Zn ₂
Formula weight [g mol ⁻¹]	1287.62	985.26	1219.65	1172.76
Crystal system	triclinic	monoclinic	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	12.621(5)	8.584(5)	9.8490(1)	9.981(5)
<i>b</i> [Å]	13.122(5)	18.854(5)	10.4408(1)	10.458(5)
<i>c</i> [Å]	18.940(5)	13.105(5)	12.1340(2)	11.968(5)
<i>a</i> [°]	76.283(5)	90	76.178(1)	76.824(5)
<i>β</i> [°]	76.145(5)	98.793(5)	74.267(1)	74.183(5)
<i>γ</i> [°]	62.922(5)	90	84.505(1)	85.209(5)
<i>V</i> [Å ³]	2681.7(16)	2096.0(16)	1165.62(3)	1170.0(9)
<i>Z</i>	2	2	1	1
<i>ρ</i> _{calcd.} [g cm ⁻³]	1.595	1.561	1.738	1.664
<i>μ</i> [mm ⁻¹]	0.811	0.725	1.233	1.141
Temperature [K]	83(2)	83(2)	83(2)	83(2)
<i>F</i> (000)	1304	1014	618	588
Crystal colour and shape	purple-blue prism	blue needle	green block	colourless plate
Crystal size [mm ³]	0.32 × 0.18 × 0.18	0.21 × 0.16 × 0.12	0.48 × 0.34 × 0.28	0.30 × 0.25 × 0.12
<i>θ</i> _{min.} / <i>θ</i> _{max.} [°]	1.12/27.25	1.91/25.72	1.79/27.15	1.81/25.63
<i>h</i>	−15 → 16	−10 → 10	−12 → 12	−12 → 12
<i>k</i>	−16 → 16	−23 → 22	−12 → 13	−12 → 12
<i>l</i>	−24 → 24	−15 → 15	0 → 15	−14 → 14
Reflections collected	27141	18555	11913	10501
Independent reflections	11701 [<i>R</i> (int) = 0.0445]	3987 [<i>R</i> (int) = 0.0475]	5077 [<i>R</i> (int) = 0.0225]	4334 [<i>R</i> (int) = 0.0771]
Completeness to <i>θ</i> _{max.} [%]	97.4	99.8	98.0	98.2
Data/restraints/parameters	11701/0/763	3987/0/297	5077/0/343	4334/0/343
GOF	1.077	1.132	1.047	0.975
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0485/0.1070	0.0405/0.0815	0.0333/0.0875	0.0622/0.1561
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0716/0.1200	0.0537/0.0884	0.0379/0.0911	0.0826/0.1663
Absolute structure factor				
Max. peak/hole [e·Å ⁻³]	0.906/−0.662	0.352/−0.401	0.820/−0.868	1.647/−1.462

other 4 hours during which time a colourless precipitate formed. The solid was filtered off and washed with MeCN. Drying in vacuo gave 345 mg (ca. 60%) of $\text{Zn}^{\text{II}}(\text{pldpt})_2(\text{BF}_4)_4(\text{MeCN})_m(\text{H}_2\text{O})_n$ (**16**) as a colourless powder. The solvent content of the initial products varied considerably from batch to batch. Heating of the powders at 60 °C in vacuo for several days similarly afforded materials of variable solvent content. A sample analysing as $\text{Zn}^{\text{II}}(\text{pldpt})_2(\text{BF}_4)_4(\text{H}_2\text{O})_2$ was used for characterisation purposes. $\text{C}_{32}\text{H}_{28}\text{B}_4\text{F}_{16}\text{N}_{12}\text{O}_2\text{Zn}_2$ (1090.63): calcd. C 35.24, H 2.59, N 15.41; found C 35.13, H 2.58, N 15.33. IR (KBr): $\tilde{\nu}$ = 1609, 1576, 1546, 1526, 1518, 1477, 1442, 1400, 1355, 1298, 1264, 1192, 1073, 911, 862, 797, 766, 750, 727, 706, 653, 640, 563, 533, 522, 436, 412 cm^{-1} . ESI-MS (pos., MeCN): m/z = 289.1 [(pldpt)H]⁺, 320.1 [Zn(pldpt)₂]²⁺, 340.6 [Zn(pldpt)₂(MeCN)]²⁺, 464.2 [Zn(pldpt)₃]²⁺, 727.2 [Zn(pldpt)₂(BF₄)]⁺. Molar conductivity (MeCN): Λ_m = 475 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Molar conductivity (DMF): Λ_m = 270 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Vapour diffusion of Et₂O into the colourless MeCN mother liquor or a colourless solution of complex **16** in MeCN afforded colourless crystals of $[\text{Zn}^{\text{II}}_2(\text{pldpt})_2(\text{MeCN})_2(\text{H}_2\text{O})_2](\text{BF}_4)_4$ (**17**).

X-ray Crystallography: X-ray data (Table 6) were collected with a Bruker SMART CCD area detector using graphite-monochromated Mo- K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods with SIR-92^[76] or SHELXS-97^[77,78] and refined against F^2 using all data by full-matrix least-squares techniques with SHELXL-97.^[79] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms, except H(101) and H(102) of the axial H₂O co-ligands in complexes **5**, **8**, **14** and **17**, were placed at calculated positions using a riding model with thermal parameters 1.2 times the equivalent isotropic thermal parameter of the atom to which they were bonded. The hydrogen atoms of the H₂O co-ligands in complexes **8**, **14** and **17** were located from the difference maps and allowed to refine freely. For complex **5** they were placed in calculated positions and subsequently fixed in their respective positions with thermal parameters 1.2 times the equivalent isotropic thermal parameter of the atom to which they were bonded. Further details of the refinement of the structures and the modelling of the disordered ClO₄[−] counterions and Et₂O solvate in complex **5** can be found in the respective CIF files. CCDC-277057 (for **3**), -277058 (for **5**), -277059 (for **6**), -277060 (for **8**), -277061 (for **11**), -277062 (for **13**), -277063 (for **14**) and -277064 (for **17**) contain 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.

Supporting Information (see also the footnote on the first page of this article): A PDF file (six pages) with supporting information for this article is available on the WWW under <http://www.eurjic.org> or from the authors. It contains a view of the asymmetric unit of ligand **3** (Figure S1), an overlay of the two crystallographically independent molecules within the asymmetric unit of ligand **3** (Figure S2), views of the molecular structures of the cations of complexes **8**, **11** and **17** (Figure S3, S4 and S5, respectively), comparisons of the ¹H and ¹³C NMR spectra, respectively, of ligand **3** and complex **15** (Figures S6 and S7, respectively) and the curves for the molar magnetic susceptibilities and effective magnetic moments of complexes **7** and **10** over the range 300–4.2 K (Figures S8 and S9, respectively).

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