Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Coordination Chemistry Reviews 241 (2003) 119–132

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

The coordination chemistry of 4-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles and related ligands

Marco H. Klingele, Sally Brooker *

Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand

Received 16 December 2002; accepted 14 March 2003

Contents

Abstract

The coordination chemistry of 4-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles, as well as of the related ligands 2,5-di(2-pyridyl)-1,3,4-oxadiazole and 2,5-di(2-pyridyl)-1,3,4-thiadiazole, is comprehensively reviewed. Literature surveys of the known 4-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles and their complexes are provided, selected representative examples are presented and the various coordination modes that have been observed in complexes of these potentially dinucleating ligands are discussed.

Keywords: 1,2,4-Triazole; 1,3,4-Oxadiazole; 1,3,4-Thiadiazole; Bridging ligand; Binding mode; Spin crossover

1. Introduction

The use of the 1,2,4-triazole moiety as a part of ligand systems has gained considerable attention in recent years [1]. This is mainly because of the fact that its ligand strength is in the right region to give spin crossover compounds with iron(II) salts. The 1,2,4-triazole system is also of magnetochemical interest because it is able to act as a bridge between metal centres thus mediating exchange coupling. In addition, it represents a hybrid of

---

Abbreviations: Ac, acetyl; Ph, phenyl; biq, 2,2′-biquinoline; bpy, 2,2′-bipyridine; cod, 1,5-cyclooctadiene; dpox, 2,5-di(2-pyridyl)-1,3,4-oxadiazole; dptd, 2,5-di(2-pyridyl)-1,3,4-thiadiazole; mmdpt, 4-(3-methylphenyl)-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole; modpt, 4-(4-methoxyphenyl)-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole; nbd, bicyclo[2.2.1]heptadiene; NHdpt, anion of 4-amino-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole; NH_2dpt, 4-amino-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole; Odpt, anion of 4-hydroxy-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole; OHdpt, 4-hydroxy-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole; pdz, pyridazine; phen, 1,10-phenanthroline; pldpt, 3,5-di(2-pyridyl)-4-(1-pyrrolyl)-4*H*-1,2,4-triazole; pmdpt, 4-(4-methylphenyl)-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole; ppy, anion of 2-phenylpyridine; pyr, pyridine; TCNQ, anion of 7,7,8,8-tetracyanoquinodimethane; tfb, 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene; trz, 1,2,4-triazole.

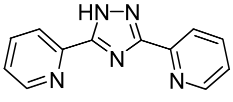
* Corresponding author. Tel.: +64-3-479-7919; fax: +64-3-479-7906.
E-mail address: sbrooker@alkali.otago.ac.nz (S. Brooker).

0010-8545/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0010-8545(03)00049-3

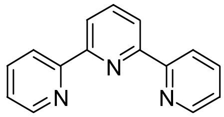
pyrazole and imidazole with regard to the arrangement of its three heteroatoms thus promising a rich and versatile coordination chemistry [1].

A common strategy to gain some control of the coordination behaviour of small heteroatom rich systems like 1,2,4-triazole is to introduce rigid substituents carrying additional donor atoms thus creating bi- or terdentate binding sites which enhance the stability of the resulting complexes due to the chelate effect. Arguably the simplest and most widely used substituent for this purpose is the 2-pyridyl group.

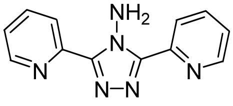
In 1965, Geldard and Lions reported the synthesis of 3,5-di(2-pyridyl)-1*H*-1,2,4-triazole (**I**) which they had prepared in connection with their work on terdentate chelating agents as an analogue of 2,2′:6′,2″-terpyridine (**II**) [2]. One of the two methods described by these authors for the synthesis of triazole **I** was the deamination of 4-amino-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole (**III**), the first practicable synthesis of which had been described a few years earlier by Dallacker [3]. With compounds **I** and **III** the first two members of a new class of ligands, the 3,5-di(2-pyridyl)-1,2,4-triazoles, had been prepared. It was, however, not until the mid 1980s that the coordination chemistry of triazoles **I** [4,5] and **III** [6] was investigated for the first time. These ligands have since been the subject of numerous studies and other related 4-substituted systems have been synthesised.



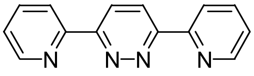
I



II



III

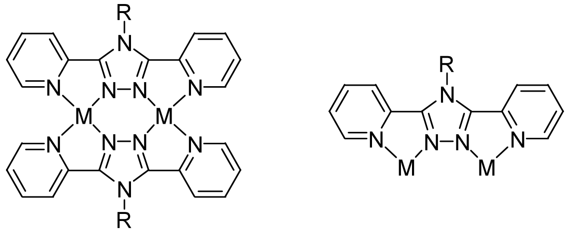


IV

The proton attached to the central triazole ring of compound **I** makes it prone to deprotonation. Thus, on reaction with metal salts, triazole **I** usually acts as an anionic ligand. A substituent on N^4, other than a hydrogen atom, removes the possibility of deprotonation of the triazole ring and the resulting ligands are neutral, unless the N^4 substituent itself can be deprotonated. With their two bidentate binding sites 3,5-di(2-pyridyl)-1,2,4-triazoles are potentially able to coordinate two metal ions and to bridge them by means of the N^1–N^2 unit of the central triazole ring. Due to the central five-membered ring the pyridine–triazole–pyridine angle is not 180° which makes 4-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles angular analogues of the linear 3,6-di(2-pyridyl)pyridazine (**IV**).

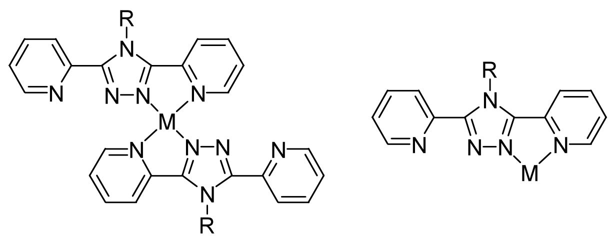
Depending on the metal-to-ligand molar ratio, the donor atoms involved in the coordination and the actual coordination geometries a variety of coordination modes are possible. In order to unequivocally distinguish between them it is first of all necessary to introduce a consistent labelling system for the relevant donor atoms. In accordance with the generally accepted numbering scheme, the two adjacent nitrogen atoms of the central triazole ring are denominated as N^1 and N^2 while the isolated nitrogen atom is N^4. The pyridine nitrogen neighbouring N^1 is denominated as N', the pyridine nitrogen next to N^2 is N''. To illustrate the nomenclature used in this review some general examples of possible coordination modes are shown in Fig. 1.

The objective of this article is to give a comprehensive overview of the availability and general coordination chemistry of 4-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles and related neutral ligands covering the literature published up until the end of November 2002. For details of the versatile coordination chemistry of triazole **I** and properties of its complexes the reader is



dinuclear $(N',N^1,N^2,N'')_2$ double bridging

dinuclear N',N^1,N^2,N'' single bridging



mononuclear $(N',N^1)_2$

mononuclear N',N^1

Fig. 1. Some general examples of possible coordination modes of complexes incorporating 4-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles as ligands. In the actual complexes the metal centres bind a number of additional co-ligands according to the respective coordination geometries.

referred to the works of J.G. Haasnoot and J. Reedijk (Leiden University, Holland), J.G. Vos (Dublin City University, Ireland), and collaborators [7–21].

2. 4-Amino-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole

Haasnoot and co-workers were the first to use readily available 4-amino-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole (NH_2dpt, **III**) for the preparation of coordination compounds [6]. They found that the reaction of this ligand with cobalt(II) and nickel(II) salts in a 1:1 molar ratio in ethanol/water produces dinuclear complexes of a 2:2 composition. The structural characterisation of one of these complexes, namely the light blue complex $[Ni^{II}_2(NH_2dpt)_2Cl_2(H_2O)_2]Cl_2 \cdot 4H_2O$ (**10**), revealed that the two nickel ions are doubly triazole-bridged. Each nickel ion is coordinated by two pyridine and two triazole nitrogens as well as a water molecule and a chloride ion, completing the distorted octahedral coordination sphere about the metal centres (Fig. 2) [6]. In this dinuclear $(N',N^1,N^2,N'')_2$ double bridging coordination mode the metal–ligand entity is almost planar. Certain deformations occur within the ligand molecules to accommodate the two nickel ions which are 4.1348(3) Å apart. The Ni–N_{pyr} distances are significantly longer than the Ni–N_{trz} distances [2.155(1)–2.164(1) and 2.013(1)–2.029(1) Å, respectively] reflecting the consequence of incorporating a five-membered instead of a six-membered ring as the link between the two pyridine rings. While there is no analogous nickel(II) complex of 3,6-di(2-pyridyl)pyridazine (**IV**), the corresponding mean Ni–N_{pyr} and Ni–N_{pdz} distances in related complexes of pyridazine **IV** are in the range of 2.05–2.12 and 2.04–2.08 Å, respectively [22–24], and Ni···Ni separations of 3.42–3.62 Å are observed [23,24]. In complex **10** the triazole bridges facilitate only weak antiferromagnetic coupling ($J = -12.5$ cm^{-1}) between the two nickel ions, while in the related cobalt(II) complexes $[Co^{II}_2(NH_2dpt)_2Cl_2(H_2O)_2]Cl_2 \cdot 4H_2O$ (**7**) and $[Co^{II}_2(NH_2dpt)_2Br_2(H_2O)_2]Br_2 \cdot 4H_2O$ (**8**) and the nickel(II) complex $[Ni^{II}_2(NH_2dpt)_2(H_2O)_4](BF_4)_4$ (**11**) the coupling constants are even smaller (-4.0, -4.2 and -9.0 cm^{-1}, respectively) [6].

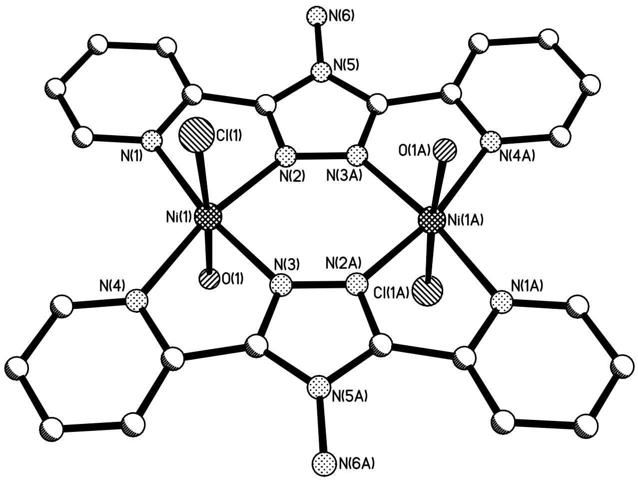


Fig. 2. Molecular structure of $[Ni^{II}_2(NH_2dpt)_2Cl_2(H_2O)_2]^{2+}$, the cation of complex **10**, featuring the dinuclear $(N',N^1,N^2,N'')_2$ double bridging coordination mode. Hydrogen atoms have been omitted for clarity. This figure was generated from data obtained from the Cambridge Crystallographic Data Centre as published originally in Ref. [6].

Interestingly, the reaction of triazole **III** with $MnBr_2 \cdot 4H_2O$ in a 1:1 molar ratio in methanol/water did not produce a dinuclear 2:2 complex as had been observed earlier for nickel(II) and cobalt(II) [25]. Instead the yellow complex $[Mn^{II}(NH_2dpt)_2(H_2O)_2]Br_2$ (**1**) was obtained in which the manganese ion is octahedrally coordinated by two triazole and two pyridine nitrogen atoms in the equatorial positions and water molecules in the axial positions resulting in a mononuclear *trans*-$(N',N^1)_2$ coordination mode with respect to the two triazole ligands (Fig. 3) [25]. This coordination mode is the one most commonly found in complexes of triazole **III** and is realised with many different metals if a metal-to-ligand molar ratio of 1:2 is used for the preparation of the coordination compounds [26–31]. However, as seen here, for instance, it can also occur when a 1:1 molar ratio is employed [25].

The influence of axial co-ligands, other than water molecules or halide ions, on the properties of octahedral complexes featuring the mononuclear *trans*-$(N',N^1)_2$ coordination mode has been studied in more detail than for any other coordination mode found in complexes of triazole **III** [26,28,30–33]. Haasnoot and co-workers prepared a series of first row transition metal complexes with the general formula $[M^{II}(NH_2dpt)_2(TCNQ)_2]$ (M = Mn, Fe, Co, Ni, Cu and Zn) incorporating the radical anion of 7,7,8,8-tetracyanoquinodimethane (TCNQ) as the axial co-ligands [26,28]. The

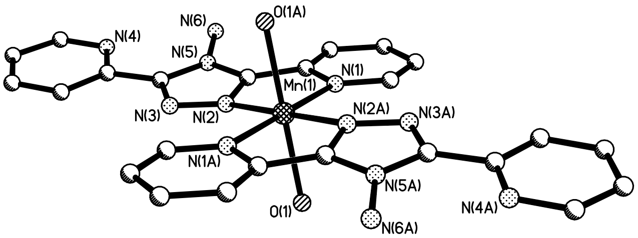


Fig. 3. Molecular structure of $[Mn^{II}(NH_2dpt)_2(H_2O)_2]^{2+}$, the cation of complex **1**, featuring the common *trans*-$(N',N^1)_2$ coordination mode. Hydrogen atoms have been omitted for clarity. This figure was generated from data obtained from the Cambridge Crystallographic Data Centre as published originally in Ref. [25].

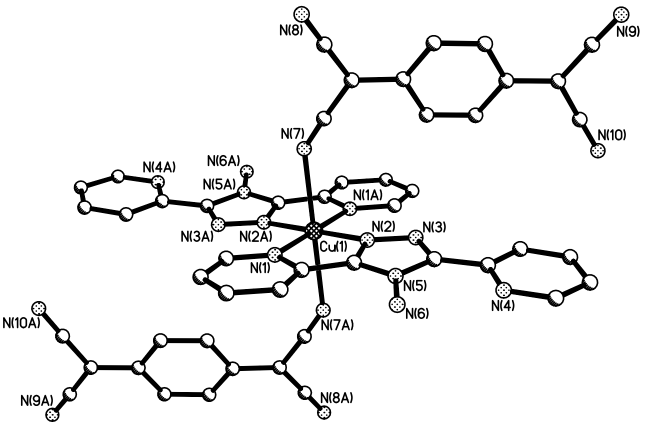


Fig. 4. Molecular structure of [$Cu^{II}(NH_2dpt)_2(TCNQ)_2$] (**13**). Hydrogen atoms have been omitted for clarity. This figure was generated from data obtained from the Cambridge Crystallographic Data Centre as published originally in Ref. [26].

molecular structure of [$Cu^{II}(NH_2dpt)_2(TCNQ)_2$] (**13**) [26] is shown in Fig. 4.

Magnetic studies on the black complex [$Fe^{II}(NH_2dpt)_2(TCNQ)_2$] (**3**) [26,28] in the temperature range of 7–460 K revealed that this compound shows a gradual high-spin ($S = 2$)↔low-spin ($S = 0$) transition with $T_{1/2}$ being about 280 K [28]. No thermal hysteresis is observed, the $\chi_M T$ versus T curves in the cooling and the heating mode are identical. The X-ray crystal structure analysis of complex **3** was carried out at 298 and 100 K. The Fe–N_{trz}, Fe–N_{pyr} and Fe–N_{TCNQ} bond lengths [2.08(1), 2.12(1) and 2.16 Å, respectively] for the high-spin (298 K) isomer **3a** were found to be significantly longer than those observed for the low-spin (100 K) isomer **3b** [2.00(2), 2.02(1) and 1.93(1) Å, respectively] thus providing further evidence of the spin crossover behaviour of this compound [28].

The corresponding isostructural pink complexes [$Fe^{II}(NH_2dpt)_2(SCN)_2$] (**4**) and [$Fe^{II}(NH_2dpt)_2(SeCN)_2$] (**5**) show spin crossover behaviour similar to that of complex **3** with $T_{1/2}$ being about 185 and 224 K for complexes **4** and **5**, respectively [30,32]. In both cases the spin transitions are gradual and thermal hystereses are not observed. The pseudohalogeno co-ligands are *N*-bound which results in a distorted octahedral N_6 coordination sphere about the iron centres. The solid state structures of complexes **4** and **5** were determined for the high-spin state at 293 K by X-ray crystallography [32]. Compared to high-spin [$Fe^{II}(NH_2dpt)_2$-$(TCNQ)_2$] (**3a**), both the Fe–N_{trz} and the Fe–N_{pyr} distances of complexes **4** and **5** are longer while their Fe–N_{XCN} distances are shorter than the corresponding Fe–N_{TCNQ} bond length in complex **3a**.

Recently Real and co-workers reported the synthesis, structural characterisation and magnetic properties of the orange complex [$Fe^{II}(NH_2dpt)_2\{N(CN)_2\}_2$] (**6**) [31], in which dicyanamido co-ligands occupy the axial positions of the FeN_6 octahedron. Complex **6** is the first spin crossover material incorporating dicyanamide ions and it also exhibits one of the lowest $T_{1/2}$ values observed in iron(II) spin crossover compounds (about 86 K).

The reaction of $CuSO_4 \cdot 5H_2O$ and triazole **III** in a metal-to-ligand molar ratio of 2:1 in methanol/water afforded the light blue complex [$Cu_2^{II}(NH_2dpt)$-$(SO_4)_2(H_2O)_4$]$\cdot H_2O$ (**14**) which was the first, and is so far the only, example of a coordination compound of triazole **III** featuring the dinuclear N',N^1,N^2,N'' single bridging coordination mode [34]. Another peculiarity of this compound is that the coordination spheres about the two copper ions are non-equivalent: while one of them is in a square-pyramidal N_2O_3 environment, the other one is centred in an N_2O_4 octahedron (Fig. 5). The Cu$\cdots$Cu separation is 4.415(1) Å and the two copper ions are bridged by, in addition to the triazole moiety, a sulfate ion. For the octahedral metal centre in complex **14** the difference between the Cu–N_{pyr} and Cu–N_{trz} bond lengths is quite small [2.061(6) and 2.038(5) Å, respectively] whereas in other octahedral complexes of triazole **III** the M–N_{pyr} distance is significantly longer than the M–N_{trz} distance. The opposite is true for the square-pyramidal copper ion in complex **14** where the Cu–N_{pyr} distance is slightly shorter than the Cu–N_{trz} distance [2.048(5) and 2.056(6) Å, respectively]. Weak antiferromagnetic coupling ($J = -34.5$ cm^{-1}) between the two copper ions is observed. To the best of our knowledge attempts to prepare similar complexes with a metal-to-ligand molar ratio of 2:1 using other metal(II) sulfates have not been made.

In the blue–green complex [$Cu^{II}(NH_2dpt)_2(H_2O)$]-$(HSO_4)_2$ (**16**), which was obtained from the reaction of $CuSO_4 \cdot 5H_2O$ and triazole **III** in a metal-to-ligand molar

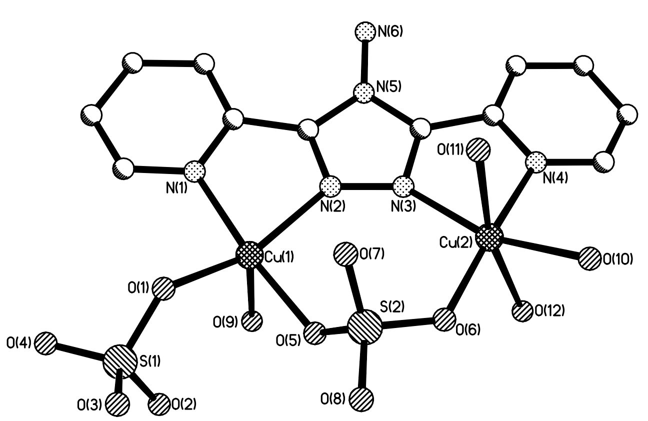


Fig. 5. Molecular structure of [$Cu_2^{II}(NH_2dpt)(SO_4)_2(H_2O)_4$]$\cdot H_2O$ (**14**). Hydrogen atoms have been omitted for clarity. The water solvate is not shown. This figure was generated from data obtained from the Cambridge Crystallographic Data Centre as published originally in Ref. [34].

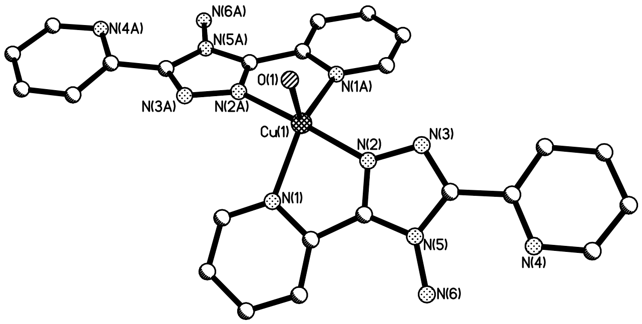
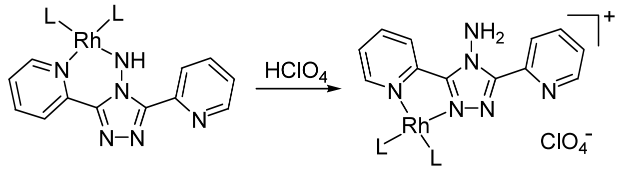


Fig. 6. Molecular structure of $[Cu^{II}(NH_2dpt)_2(H_2O)]^{2+}$, the cation of complex **16**. Hydrogen atoms have been omitted for clarity. This figure was generated from data obtained from the Cambridge Crystallographic Data Centre as published originally in Ref. [35].

ratio of 1:2 in methanol/water, the copper ion is five-coordinate and resides in a N_4O coordination sphere which is intermediate between a square-pyramidal and a trigonal-bipyramidal polyhedron (Fig. 6) [35]. Compound **16** is the only example of a mononuclear five-coordinate complex of triazole **III** and is a very rare example of a copper coordination compound containing hydrogensulfate ions. As is usually observed in complexes of this ligand, the $Cu-N_{pyr}$ distances are significantly longer than the $Cu-N_{trz}$ distances [2.066(3) and 1.958(3) Å, respectively].

Studies by Oro and co-workers showed that the amino group of triazole **III** can be deprotonated and both the resulting anion and the neutral ligand were employed in the preparation of a series of mononuclear square-planar rhodium(I) complexes containing additional co-ligands (Scheme 1) [36]. Based mainly on ^1H-NMR data they concluded that in complexes **27**–**30** with the general formula $[Rh^I(NHdpt)(diolefin)]$, incorporating the anionic ligand, the deprotonated 4-amino group, rather than N^1 of the triazole ring, is coordinated to the rhodium ion [36]. In the corresponding complexes of the neutral ligand the expected mononuclear N',N^1 coordination mode was observed as evidenced by the structural characterisation of $[Rh^I(NH_2dpt)(CO)_2]ClO_4$ (**35**) (Fig. 7). The complexes of the deprotonated ligand could be converted into their neutral ligand congeners by reacting the former with perchloric acid (Scheme 1).

With the presentation of the structural analyses of the two isomeric complexes $[Ru^{II}(NH_2dpt)(CO)_2Cl_2]$ (**23**)



Scheme 1. Coordination modes in rhodium(I) complexes of ligand **III** in its deprotonated and neutral form and their interconversion.

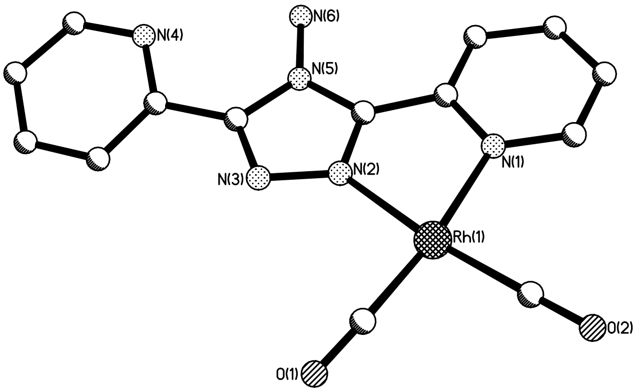


Fig. 7. Molecular structure of $[Rh^I(NH_2dpt)(CO)_2]^+$, the cation of complex **35**. Hydrogen atoms have been omitted for clarity. This figure was generated from data obtained from the Cambridge Crystallographic Data Centre as published originally in Ref. [36].

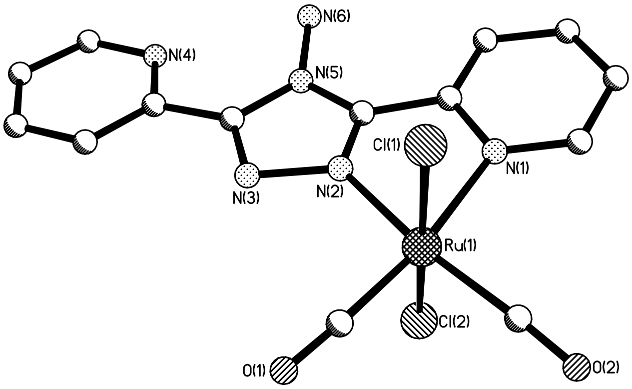


Fig. 8. Molecular structure of complex **23**, the N',N^1 isomer of $[Ru^{II}(NH_2dpt)(CO)_2Cl_2]$. Hydrogen atoms have been omitted for clarity. This figure was generated from data obtained from the Cambridge Crystallographic Data Centre as published originally in Ref. [37].

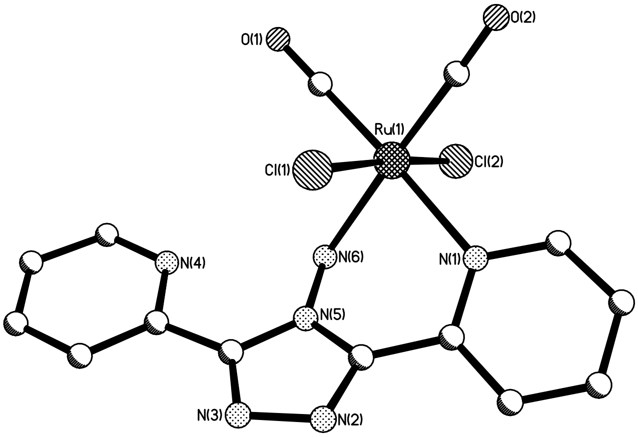
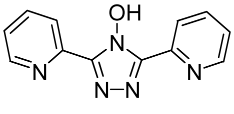


Fig. 9. Molecular structure of complex **24**, the N',N^{amine} isomer of $[Ru^{II}(NH_2dpt)(CO)_2Cl_2]$. Hydrogen atoms have been omitted for clarity. The methanol solvate is not shown. This figure was generated from data obtained from the Cambridge Crystallographic Data Centre as published originally in Ref. [37].

and $[Ru^{II}(NH_2dpt)(CO)_2Cl_2]\cdot MeOH$ (**24**) (Figs. 8 and 9, respectively) in 1993, Rheingold et al. [37] provided proof that, at least in ruthenium(II) complexes of neutral triazole **III**, a mononuclear N',N^{amine} coordination mode, as postulated earlier for rhodium(I) complexes of the deprotonated ligand [36], can indeed be realised.

It should be pointed out that the yellow complex **24**, featuring the mononuclear N',N^{amine} coordination mode, was not obtained by deliberate synthesis but crystallised spontaneously from the same reaction mixture as the orange complex **23**, the yields being 35 and 30%, respectively. Changing the halogeno co-ligands from chloride to bromide ions afforded predominantly the yellow complex $[Ru^{II}(NH_2dpt)(CO)_2Br_2]\cdot MeOH$ (**25**) along with less than 5% of an orange isomer. Complex **25** was assigned the mononuclear N',N^{amine} coordination mode based on the ^1H-NMR data and comparison of the colours of the complexes [37]. In contrast, the use of iodo co-ligands produced only the orange complex $[Ru^{II}(NH_2dpt)(CO)_2I_2]$ (**26**) which features the common mononuclear N',N^1 coordination mode. The authors attributed the occurrence of this binding isomerism to steric factors: 'coordination directly to the less sterically crowded triazole ring, rather than the amino group, is preferred for the larger halogen ligands' [37]. Similarly, these authors proposed that in the complex $[Re^I(NH_2dpt)(CO)_3Cl]$ (**39**) the larger radius of rhenium(I) over ruthenium(II) leads to the adoption of the mononuclear N',N^1 coordination mode as concluded from ^1H-NMR data [37].



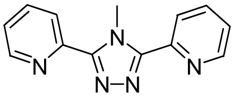
V

A recent publication by Vos and co-workers dealt with the complex $[Rh^{III}(Odpt)(phen)_2](PF_6)_2\cdot 0.767MeCN\cdot 0.28H_2O$ (**41a**) (CCDC code XIJWUI) which would formally be a derivative of 4-hydroxy-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole (OHdpt, **V**) [38]. While other 4-hydroxy-4*H*-1,2,4-triazoles are in fact known in the literature [39], triazole **V** has never been prepared in substance and its occurrence in its deprotonated form as a ligand in complex **41a** was attributed to an oxidative rhodium(III) mediated N–O bond formation in 3,5-di(2-pyridyl)-1*H*-1,2,4-triazole (**I**) in alkaline solution [38]. After publication the authors discovered, however, that the formulation of complex **41a** as a derivative of 4-hydroxy triazole **V** was incorrect and that it really incorporated 4-amino triazole **III**, which had been present as an impurity in the batch of 3,5-di(2-pyridyl)-1*H*-1,2,4-triazole **I** used in the preparation of the complex, in its deprotonated form [40]. Complex **41a** has therefore been reformulated as complex **41b** (CCDC code XIJWUI01) in which the metal–NH–triazole moiety is the same as that proposed earlier to occur in rhodium(I) complexes of the deprotonated ligand **III** (Scheme 1) [36].

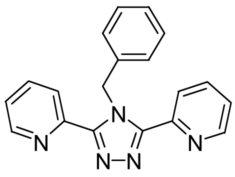
In summary, triazole **III** has been shown to give coordination compounds with all first row transition metals from manganese through to zinc as well as with ruthenium, rhodium, rhenium and iridium (Table 1). The vast majority of these complexes are mononuclear while dinuclear complexes have only been obtained with cobalt, nickel and copper. There are no reports of dinuclear complexes of any second or third row transition metal incorporating triazole **III** as a ligand. In spite of the ability of the 4-amino group of triazole **III** to coordinate to metal ions, coordination compounds where three metal centres are bridged by one ligand molecule are unknown. It is interesting to note that of the 40 reported complexes of triazole **III** (excluding complex **41b**) only 14, i.e. 35%, have been structurally characterised (Table 1). This could be an indication of relatively poor crystallisation behaviour of these coordination compounds.

3. 4-Alkyl-3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles

The only 4-alkyl-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles that have appeared in the literature are the 4-methyl [45,46] and the 4-benzyl [47] triazoles **VI** and **VII**. However, both compounds have so far been obtained only as minor by-products in the methylation and benzylation reactions of 3,5-di(2-pyridyl)-1*H*-1,2,4-triazole (**I**), respectively, and have not been isolated from the mixtures of isomers. Consequently, their coordination chemistry has not been investigated to date.



VI



VII

4. 4-Heteroaryl- and 4-aryl-3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles

The first ever 4-heteroaryl-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazole to be synthesised was 3,4,5-tri(2-pyridyl)-4*H*-1,2,4-triazole (**VIII**) [48], but no complexes of this compound have been reported. Mandal and co-workers obtained the 4-(1-pyrrolyl) triazole **IX** by reacting 4-amino triazole **III** with 2,5-dimethoxytetrahydrofuran [49–51].

Table 1
Survey of complexes of 4-amino-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole ($\mathrm{NH_2dpt}$, **III**)

Complex	Description and remarks [a]	CCDC code	Reference
$[\mathrm{Mn^{II}(NH_2dpt)_2(H_2O)_2}]\mathrm{Br_2}$ (**1**)	Octahedral, mononuclear *trans*-$(N',N^1)_2$ mode	SIJPIK	[25]
$[\mathrm{Mn^{II}(NH_2dpt)_2(TCNQ)_2}]$ (**2**)	Octahedral, mononuclear *trans*-$(N',N^1)_2$ mode	–	[28]
$[\mathrm{Fe^{II}(NH_2dpt)_2(TCNQ)_2}]$ high spin (**3a**)	Octahedral, mononuclear *trans*-$(N',N^1)_2$ mode	ZUCROE01	[26,28]
$[\mathrm{Fe^{II}(NH_2dpt)_2(TCNQ)_2}]$ low spin (**3b**)	Octahedral, mononuclear *trans*-$(N',N^1)_2$ mode	ZUCROE	[26,28]
$[\mathrm{Fe^{II}(NH_2dpt)_2(SCN)_2}]$ (**4**)	Octahedral, mononuclear *trans*-$(N',N^1)_2$ mode, *N*-bound thiocyanates	QAHVIE	[30,32,33]
$[\mathrm{Fe^{II}(NH_2dpt)_2(SeCN)_2}]$ (**5**)	Octahedral, mononuclear *trans*-$(N',N^1)_2$ mode, *N*-bound selenocyanates	QAHVOK	[30,32,33]
$[\mathrm{Fe^{II}(NH_2dpt)_2\{N(CN)_2\}_2}]$ (**6**)	Octahedral, mononuclear *trans*-$(N',N^1)_2$ mode	IBUVUW	[31]
$[\mathrm{Co_2^{II}(NH_2dpt)_2Cl_2(H_2O)_2}]\mathrm{Cl_2\cdot 4H_2O}$ (**7**)	Octahedral, dinuclear $(N',N^1,N^2,N'')_2$ double bridging mode	–	[6]
$[\mathrm{Co_2^{II}(NH_2dpt)_2Br_2(H_2O)_2}]\mathrm{Br_2\cdot 4H_2O}$ (**8**)	Octahedral, dinuclear $(N',N^1,N^2,N'')_2$ double bridging mode	–	[6]
$[\mathrm{Co^{II}(NH_2dpt)_2(TCNQ)_2}]$ (**9**)	Octahedral, mononuclear *trans*-$(N',N^1)_2$ mode	–	[26,28]
$[\mathrm{Ni_2^{II}(NH_2dpt)_2Cl_2(H_2O)_2}]\mathrm{Cl_2\cdot 4H_2O}$ (**10**)	Octahedral, dinuclear $(N',N^1,N^2,N'')_2$ double bridging mode, first structure of a $\mathrm{NH_2dpt}$ complex	DAYLAQ	[6]
$[\mathrm{Ni_2^{II}(NH_2dpt)_2(H_2O)_4}](\mathrm{BF_4})_4$ (**11**)	Octahedral, dinuclear $(N',N^1,N^2,N'')_2$ double bridging mode	–	[6]
$[\mathrm{Ni^{II}(NH_2dpt)_2(TCNQ)_2}]$ (**12**)	Octahedral, mononuclear *trans*-$(N',N^1)_2$ mode	–	[26,28]
$[\mathrm{Cu^{II}(NH_2dpt)_2(TCNQ)_2}]$ (**13**)	Octahedral, mononuclear *trans*-$(N',N^1)_2$ mode	SOZZOW	[26,28]
$[\mathrm{Cu_2^{II}(NH_2dpt)(SO_4)_2(H_2O)_4}]\mathrm{\cdot H_2O}$ (**14**)	Mixed octahedral and square-pyramidal, mononuclear N',N^1,N^2,N'' single bridging mode, additional sulfato bridge	ZIMDII	[34]
$[\mathrm{Cu^{II}(NH_2dpt)_2}](\mathrm{BF_4})_2$ (**15**)	Octahedral, mononuclear *trans*-$(N',N^1)_2$ mode, weakly coordinated tetrafluoroborates in axial positions	TUDJOR	[29]
$[\mathrm{Cu^{II}(NH_2dpt)_2(H_2O)}](\mathrm{HSO_4})_2$ (**16**)	Intermediate between square-pyramidal and trigonal-bipyramidal, mononuclear pseudo-*trans*-$(N',N^1)_2$ mode, hydrogensulfates as counterions	LIVMEI	[35]
$[\mathrm{Zn^{II}Cl_2\ NH_2dpt}]_n$ (**17**)		–	[27]
$[\mathrm{Zn^{II}(NO_3)_2(NH_2dpt)_2}]$ (**18**)		–	[27]
$[\mathrm{Zn^{II}(NH_2dpt)_2(H_2O)_2}](\mathrm{ClO_4})_2$ (**19**)	Octahedral, mononuclear *trans*-$(N',N^1)_2$ mode	ZOCYIZ	[27]
$[\mathrm{Zn^{II}(NH_2dpt)_2(TCNQ)_2}]$ (**20**)	Octahedral, mononuclear *trans*-$(N',N^1)_2$ mode	–	[28]
$[\mathrm{Ru^{II}(NH_2dpt)(bpy)_2}](\mathrm{PF_6})_2$ (**21**)		–	[41]
$[\mathrm{Ru^{II}(NH_2dpt)(biq)_2}](\mathrm{PF_6})_2$ (**22**)		–	[41]
$[\mathrm{Ru^{II}(NH_2dpt)(CO)_2Cl_2}]$ (**23**)	Octahedral, mononuclear N',N^1 mode, isomer of complex **24**	LECBAW	[37]
$[\mathrm{Ru^{II}(NH_2dpt)(CO)_2Cl_2}]\mathrm{\cdot MeOH}$ (**24**)	Octahedral, mononuclear N',N^{amine} mode, isomer of complex **23**, first structure featuring this unusual coordination mode	LECBEA	[37]
$[\mathrm{Ru^{II}(NH_2dpt)(CO)_2Br_2}]\mathrm{\cdot MeOH}$ (**25**)	Octahedral, mononuclear N',N^{amine} mode, analogous to complex **24**	–	[37]
$[\mathrm{Ru^{II}(NH_2dpt)(CO)_2I_2}]$ (**26**)	Octahedral, mononuclear N',N^1 mode, analogous to complex **23**	–	[37]
$[\mathrm{Rh^{I}(NHdpt)(tfb)}]$ (**27**)	Square-planar, mononuclear N',N^{amine} mode	–	[36]
$[\mathrm{Rh^{I}(NHdpt)(cod)}]$ (**28**)	Square-planar, mononuclear N',N^{amine} mode	–	[36]
$[\mathrm{Rh^{I}(NHdpt)(nbd)}]$ (**29**)	Square-planar, mononuclear N',N^{amine} mode	–	[36]
$[\mathrm{Rh^{I}(NHdpt)(CO)(PPh_3)}]\mathrm{\cdot 0.5CH_2Cl_2}$ (**30**)	Square-planar, mononuclear N',N^{amine} mode	–	[36]
$[\mathrm{Rh^{I}(NH_2dpt)(tfb)}]\mathrm{ClO_4}$ (**31**)		–	[36]
$[\mathrm{Rh^{I}(NH_2dpt)(cod)}]\mathrm{ClO_4}$ (**32**)		–	[36]
$[\mathrm{Rh^{I}(NH_2dpt)(nbd)}]\mathrm{ClO_4}$ (**33**)		–	[36]
$[\mathrm{Rh^{I}(NH_2dpt)(CO)(PPh_3)}]\mathrm{ClO_4}$ (**34**)		–	[36]
$[\mathrm{Rh^{I}(NH_2dpt)(CO)_2}]\mathrm{ClO_4}$ (**35**)	Square-planar, mononuclear N',N^1 mode, dimeric units with weak Rh···Rh interactions	FEKJOU	[36]
$[\mathrm{Rh^{I}(NH_2dpt)(tfb)Cl}]$ (**36**)		–	[36]
$[\mathrm{Rh^{I}(NH_2dpt)(nbd)Cl}]$ (**37**)		–	[36]
$[\mathrm{Rh^{III}(NH_2dpt)(ppy)_2}]\mathrm{PF_6}$ (**38**)		–	[42]
$[\mathrm{Re^{I}(NH_2dpt)(CO)_3Cl}]$ (**39**)	Octahedral, mononuclear N',N^1 mode	–	[37]
$[\mathrm{Ir^{III}(NH_2dpt)(ppy)_2}]\mathrm{PF_6}$ (**40**)		–	[42–44]

[a] For complexes where no X-ray crystallographic data are available comments on the structure are based on spectroscopic data, chemical reactivity and comparison with related compounds as discussed in the original publications.

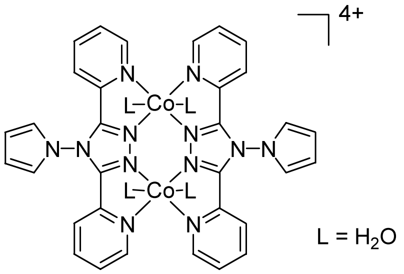
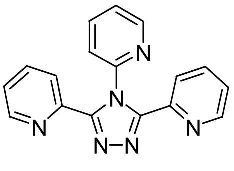


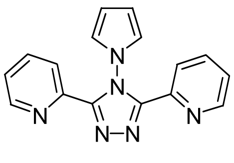
Fig. 10. Structural drawing of $[Co^{II}_2(pldpt)_2(H_2O)_4]^{2+}$, the cation of complex **45**.

Table 2
Survey of 4-heteroaryl- and 4-aryl-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles that have appeared in the literature

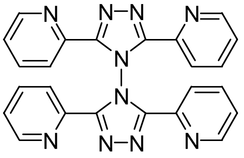
Substituent on N^4	Abbreviation	CCDC code	Reference
2-Pyridyl (**VIII**)		–	[48]
1-Pyrrolyl (**IX**)	pldpt	–	[49,53]
Phenyl (**XI**)		MATKOH	[48,55,65]
4-Chlorophenyl (**XII**)		NIFJUH	[56]
4-Bromophenyl (**XIII**)		NUBCES	[57]
4-Methoxyphenyl (**XIV**)	modpt	HIYFAW	[58–60]
4-Methylphenyl (**XV**)	pmdpt	QAYVOB	[61–64]
3-Methylphenyl (**XVI**)	mmdpt	–	[64]



VIII



IX



X

The reaction of 3,5-di(2-pyridyl)-4-(1-pyrrolyl)-4*H*-1,2,4-triazole (pldpt, **IX**) with $CoCl_2 \cdot 6H_2O$ in a 1:1 molar ratio in methanol/water produced the orange complex $[Co^{II}_2(pldpt)_2(H_2O)_4]Cl_4 \cdot 2MeOH \cdot 2H_2O$ (**45**) [49] featuring the dinuclear $(N',N^1,N^2,N'')_2$ double bridging mode (Fig. 10) which had been observed earlier for cobalt and nickel complexes of 4-amino triazole **III** [6]. The pyrrole rings in complex **45** are tilted with respect to the triazole rings and the two cobalt centres are 4.226(2) Å apart [49]. Unfortunately, further structural information is not available as the atomic coordinates for this structure did not appear in the original publication and were never deposited with the Cambridge Crystallographic Data Centre [52]. Reductive electropolymerisation of complex **45** produced a conductive metallopolymer [49,53] which was shown by ^{1}H-NMR to contain 4,4′-bis[3,5-di(2-pyridyl)-4*H*-1,2,4-triazole] (**X**) [53]. No other coordination compounds of 4-(1-pyrrolyl) triazole **IX** have appeared in the literature.

Employing the methodology developed by Klingsberg [54], You and coworkers recently prepared the 4-phenyl [55], 4-(4-chlorophenyl) [56], 4-(4-bromophenyl) [57], 4-(4-methoxyphenyl) [58–60], 4-(4-methylphenyl) [61–64] and 4-(3-methylphenyl) [64] triazoles **XI**–**XVI**. The synthesis of 4-phenyl triazole **XI** has also been reported by other methods [48,65]. A complete list of all known 4-

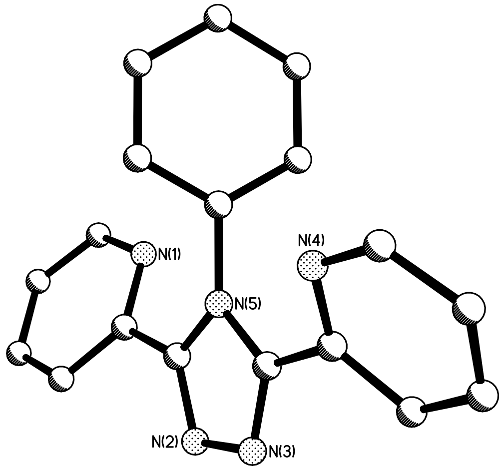


Fig. 11. Molecular structure of 4-phenyl-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole (**XI**). Hydrogen atoms have been omitted for clarity. This figure was generated from data obtained from the Cambridge Crystallographic Data Centre as published originally in Ref. [55].

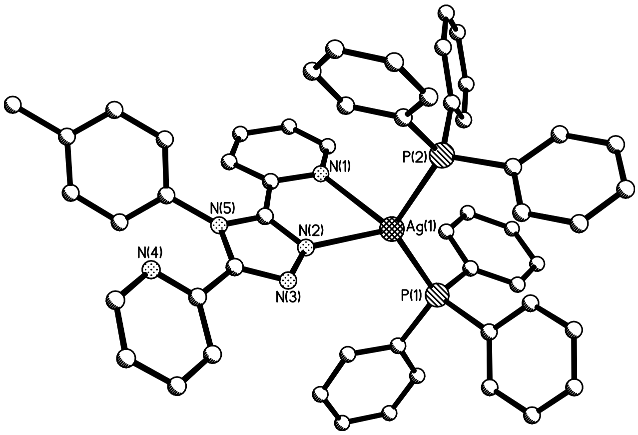
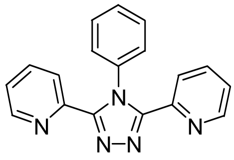
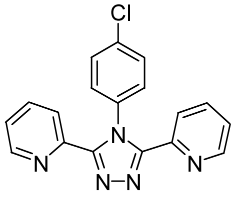


Fig. 12. Molecular structure of $[Ag^I(pmdpt)(PPh_3)_2]^+$, the cation of complex **50**. Hydrogen atoms have been omitted for clarity. This figure was generated from data obtained from the Cambridge Crystallographic Data Centre as published originally in Ref. [61].

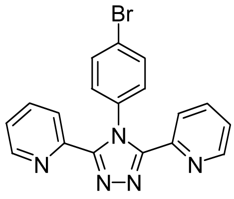
heteroaryl- and 4-aryl-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles is given in Table 2.



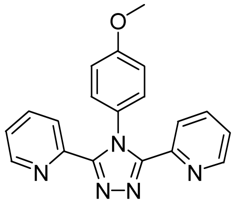
XI



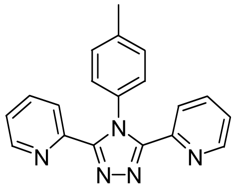
XII



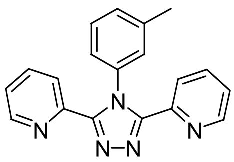
XIII



XIV



XV



XVI

The X-ray crystal structure analyses of the free ligands **XI**–**XV** [55–58,63] revealed that in all cases both pyridine rings are tilted with respect to the triazole ring by 26.91(8)–48.0(3)° with the pyridine nitrogen atoms being on opposite sides of the triazole mean plane. The phenyl rings on N^4 are also inclined relative to the triazole ring by angles of 53.8(2)–88.37(5)°. The pyridine nitrogen atoms do not face in the same direction as the N^1 and N^2 atoms of the triazole rings but towards the phenyl rings. As a representative example, the molecular structure of 4-phenyl triazole **XI** is shown in Fig. 11.

The first coordination compound of a 4-aryl-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazole was the complex $[Ag^I(pmdpt)(PPh_3)_2]ClO_4$ (**50**) whose structural analysis was published in 1999 (Fig. 12) [61]. Once again the mononuclear N',N^1 coordination mode is observed with the common trend of longer $M-N_{pyr}$ than $M-N_{trz}$ bonds being particularly noticeable [2.548(2) and 2.308(2) Å, respectively]. As a result of the presence of the two bulky triphenylphosphane co-ligands in addition to the chelating 4-(4-methylphenyl) triazole **XV**, the tetrahedral N_2P_2 coordination sphere about the silver ion is strongly distorted.

Coordination compounds of 4-(4-methylphenyl) triazole (**XV**) with a metal-to-ligand molar ratio of 1:2 have also been prepared [62–64]. The light brown complex $[Co^{II}(pmdpt)_2(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ (**47**) [63] and the pale purple complex $[Ni^{II}(pmdpt)_2(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ (**49**) [62,63] are isostructural and feature the octahedral mononuclear *trans*-$(N',N^1)_2$ coordination mode. In spite of reacting the metal salt with ligand **XV** in a 1:1 molar ratio only these mononuclear species could be isolated. The overall architecture of the respective complex cations is identical to that of complex $[Mn^{II}(NH_2dpt)_2(H_2O)_2]Br_2$ (**1**) of 4-amino triazole (**III**) (Fig. 3) reported by Haasnoot and co-workers [25]. A comparison of the Ni–N bond lengths of complex **49** [62,63] with those of $[Ni^{II}_2(NH_2dpt)_2Cl_2(H_2O)_2]Cl_2 \cdot 4H_2O$ (**10**) [6] shows that in the mononuclear complex **49** the $Ni-N_{pyr}$ distances [2.117(4) Å] are about 0.04–0.05 Å shorter than those in the dinuclear complex **10**. At the same time the $Ni-N_{trz}$ bond lengths in complex **49** [2.052(4) Å] are about 0.02–0.04 Å longer than those in the dinuclear complex **10**.

The inability of 4-(4-methylphenyl) triazole (**XV**) to form dinuclear 2:2 complexes with cobalt(II) and nickel(II) salts [63] is somewhat surprising as 4-amino triazole (**III**) [6] and 4-(1-pyrrolyl) triazole **IX** [49] are able to do so. This phenomenon can hardly be explained simply on the basis of steric effects. Introduction of a bulky N^4 substituent like a phenyl ring should tend to have the inverse effect and rather facilitate the dinuclear $(N',N^1,N^2,N'')_2$ double bridging mode as the substituent is expected to push the two pyridine substituents somewhat further towards the N^1-N^2 unit of the triazole ring thus bringing the pyridine–triazole–pyridine moiety slightly closer to linearity. While the actual reason for this peculiarity remains unknown at this point, it seems plausible that the N^4 substituent influences the ligand reactivity by electronic effects.

The first iron(II) complexes of any 4-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazole other than the 4-amino triazole **III** were recently reported by You and co-workers [64]. The red-brown complex $[Fe^{II}(pmdpt)_2$-

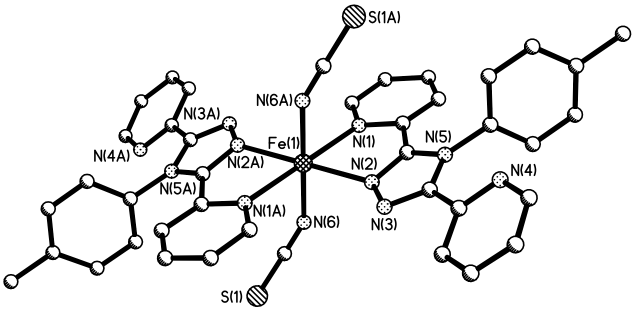


Fig. 13. Molecular structure of $[Fe^{II}(pmdpt)_2(SCN)_2]$ (**43**). Hydrogen atoms have been omitted for clarity. This figure was generated from data obtained from the Cambridge Crystallographic Data Centre as published originally in Ref. [64].

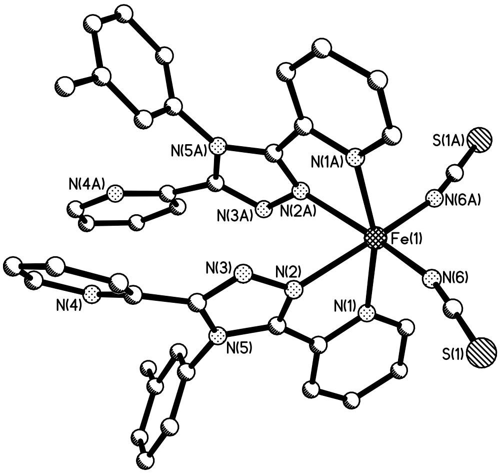


Fig. 14. Molecular structure of [$Fe^{II}(mmdpt)_2(SCN)_2$] (**44**). Hydrogen atoms have been omitted for clarity. This figure was generated from data obtained from the Cambridge Crystallographic Data Centre as published originally in Ref. [64].

$(SCN)_2$] (**43**) of the 4-(4-methylphenyl) triazole (**XV**) features the common mononuclear *trans*-(N',N^1)$_2$ coordination mode with *N*-bound thiocyanate ions in the axial positions (Fig. 13) [64]. Unlike the related complexes [$Fe^{II}(NH_2dpt)_2(SCN)_2$] (**4**) [32], [$Fe^{II}(NH_2dpt)_2(SeCN)_2$] (**5**) [32] and [$Fe^{II}(NH_2dpt)_2\{N(CN)_2\}_2$] (**6**) [31], all of which are derived from 4-amino triazole (**III**), complex **43** shows only slight differences between the Fe–N_{pyr} and Fe–N_{trz} bond lengths [2.213(3) and 2.192(2) Å, respectively] [64].

A fundamentally different product was obtained when 4-(3-methylphenyl) triazole **XVI**, instead of the isomeric 4-(4-methylphenyl) triazole **XV**, was reacted with $Fe(SCN)_2$ in methanol under the same reaction conditions as in the synthesis of complex **43** [64]. In the resulting red complex [$Fe^{II}(mmdpt)_2(SCN)_2$] (**44**) the metal ion resides in an octahedral N_6 environment made up of two triazole ligands and two thiocyanato co-ligands. The *cis* arrangement of these co-ligands, however, represents a coordination mode which was at that stage unprecedented in the coordination chemistry of 4-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles (Fig. 14) [64]. This dramatic consequence of the change in position of the rather small methyl substituent, which is relatively far away from the coordination site and apparently does not cause any steric hindrance, is quite remarkable. Another unusual feature of complex **44** is that the Fe–N_{pyr} bond lengths are shorter than the Fe–N_{trz} bond lengths [2.217(2) and 2.248(3) Å, respectively], presumably as a result of steric crowding.

Complexes **43** and **44** are not only very different structurally but also with respect to their magnetic properties. While [$Fe^{II}(mmdpt)_2(SCN)_2$] (**44**), featuring the mononuclear *cis*-(N',N^1)$_2$ coordination mode, retains its high-spin state in the temperature range of 75–300 K and shows Curie–Weiss behaviour, the isomeric [$Fe^{II}(pmdpt)_2(SCN)_2$] (**43**) is a spin crossover material [64]. The spin transition in complex **43** is quite abrupt with $T_{1/2}$ being about 231 K. A hysteresis loop is not observed.

The reaction of 4-(4-methoxyphenyl) triazole (**XIV**) with $Co(OAc)_2 \cdot 4H_2O$ or $Ni(OAc)_2 \cdot 4H_2O$ and $NaClO_4$ in a 2:1:2 molar ratio in ethanol yielded the isomorphous mononuclear complexes [$Co^{II}(modpt)_2(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ (**46**) and [$Ni^{II}(modpt)_2(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ (**48**), respectively [59]. These complexes feature the mononuclear *trans*-(N',N^1)$_2$ coordination mode and are very similar to the corresponding complexes **47** [63] and **49** [62,63] of 4-(4-methylphenyl) triazole (**XV**). No attempts to prepare dinuclear 2:2 complexes of 4-(4-methoxyphenyl) triazole (**XIV**) have been reported. A yellow mononuclear manganese(II) complex of ligand **XIV**, namely [$Mn^{II}(modpt)(H_2O)_2(SCN)_2$] (**42**) [60], has also been reported while there are no reports of any iron complexes of this ligand. A complete list of complexes of 4-heteroaryl- and 4-aryl-

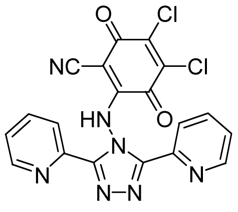
Table 3
Survey of complexes of 4-heteroaryl- and 4-aryl-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles

Complex	Description and remarks	CCDC code	Reference
[$Mn^{II}(modpt)(H_2O)_2(SCN)_2$] (**42**)	Octahedral, mononuclear N',N^1 mode, *N*-bound thiocyanates	XOKBII	[60]
[$Fe^{II}(pmdpt)_2(SCN)_2$] (**43**)	Octahedral, mononuclear *trans*-(N',N^1)$_2$ mode, *N*-bound thiocyanates	FADVUC	[64]
[$Fe^{II}(mmdpt)_2(SCN)_2$] (**44**)	Octahedral, mononuclear *cis*-(N',N^1)$_2$ mode, *N*-bound thiocyanates	FADWAJ	[64]
[$Co_2^{II}(pldpt)_2(H_2O)_4]Cl_4 \cdot 2MeOH \cdot 2H_2O$ (**45**)	Octahedral, dinuclear (N',N^1,N^2,N')$_2$ double bridging mode	LASZEK	[49,53]
[$Co^{II}(modpt)_2(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ (**46**)	Octahedral, mononuclear *trans*-(N',N^1)$_2$ mode	WONDAE	[59]
[$Co^{II}(pmdpt)_2(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ (**47**)	Octahedral, mononuclear *trans*-(N',N^1)$_2$ mode	QAYWAO	[63]
[$Ni^{II}(modpt)_2(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ (**48**)	Octahedral, mononuclear *trans*-(N',N^1)$_2$ mode	WONDEI	[59]
[$Ni^{II}(pmdpt)_2(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ (**49**)	Octahedral, mononuclear *trans*-(N',N^1)$_2$ mode	QAYVUH	[62,63]
[$Ag^{I}(pmdpt)(PPh_3)_2]ClO_4$ (**50**)	Tetrahedral, mononuclear N',N^1 mode	BEQMOZ	[61]

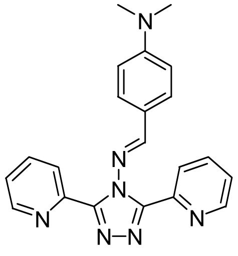
substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles is given in Table 3.

5. Derivatives of 4-amino-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole

The ready availability of 4-amino-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole (**III**) makes it an ideal starting material for the preparation of more complex ligand systems by derivatisation of the 4-amino group. This strategy was first exploited in 1991 by Lagrenee and co-workers when they prepared compound **XVII**, which has never actually been used as a ligand, by the reaction of triazole **III** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone [66]. The first coordination compounds incorporating a ligand derived from triazole **III** were two mononuclear ruthenium(II) complexes reported by Campagna and co-workers the following year [41]. In these complexes, compound **XVIII**, which had been obtained by the condensation of triazole **III** with 4-(dimethylamino)benzaldehyde, was used as the ligand [41].

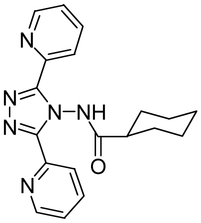


XVII

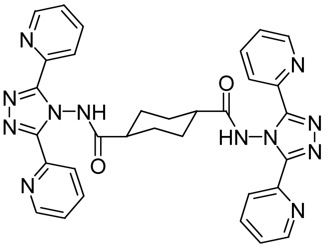


XVIII

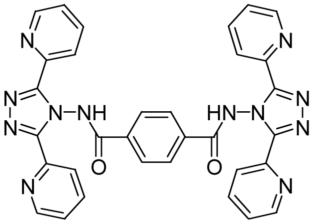
Acylation of triazole **III** using cyclohexanecarbonyl chloride gave ligand **XIX** of which a mononuclear ruthenium(II) complex and a corresponding mononuclear osmium(II) complex have been reported [67]. Similarly, the first deliberately synthesised covalently linked 4,4′-bis[3,5-di(2-pyridyl)-4*H*-1,2,4-triazole], namely ligand **XX**, was prepared using 1,4-cyclohexanedicarbonyl chloride [67]. Ligand **XX** has been employed in the synthesis of homodinuclear complexes of ruthenium(II) [67,68], osmium(II) [67] and iridium(III) [44] as well as of a heterodinuclear complex containing both a ruthenium(II) and an osmium(II) ion [69]. In the latter complex, ligand **XX** was shown to allow photoinduced intercomponent energy transfer between the two different metal centres [69]. Ligands **XXI** and **XXII** were synthesised as analogues of ligand **XX** and dinuclear ruthenium(II) complexes of these ligands have been reported [68].



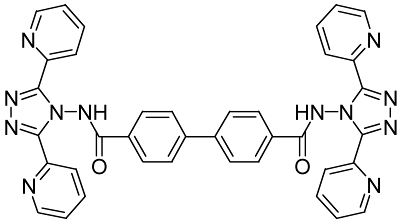
XIX



XX



XXI

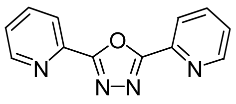


XXII

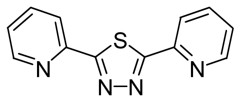
None of the above mentioned complexes have been characterised by X-ray diffraction and apparently no attempts have been made to prepare tetranuclear complexes of the covalently linked 4,4′-bis[3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles] **XX**–**XXII**. On the basis of steric considerations and the available spectroscopic data it is, however, beyond doubt that in all of these complexes each of the two potentially dinucleating triazole moieties of the respective ligand is coordinated to only one metal centre and that a dinuclear N',N^1,N^2,N'' single bridging coordination mode does not occur.

6. Related ligands

Replacement of the N^4-R unit of the 1,2,4-triazole moiety in 4-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles by other divalent units produces neutral ligands with a similar overall structure and arrangement of donor atoms. Although the resulting ligands are no longer based on the 1,2,4-triazole system, including them in this review is justified due to the obvious resemblance between the respective heterocyclic systems. While in principle a number of such divalent units are possible, only 2,5-di(2-pyridyl)-1,3,4-oxadiazole (dpox, **XXIII**) and 2,5-di(2-pyridyl)-1,3,4-thiadiazole (dptd, **XIV**) have been prepared so far and both have been used for the preparation of coordination compounds. Literature surveys of complexes of oxadiazole **XXIII** [70–74] and thiadiazole **XIV** [75] are given in Tables 4 and 5, respectively.



XXIII



XIV

The four nitrogen donors in oxadiazole **XXIII** and thiadiazole **XIV** should be somewhat closer to linearity than in related 1,2,4-triazole-based ligands due to the bigger size of the oxygen and sulfur atom compared to nitrogen incorporated into the respective heterocyclic rings. It is interesting to note, however, that the tendency of these ligands to form dinuclear 2:2 complexes is not enhanced compared to their 1,2,4-triazole-based congeners. Depending on the reaction conditions employed and the metal source used, i.e. the counterion, only mononuclear 1:1 complexes [70], mononuclear 1:2 complexes [71–75] or one-dimensional coordination polymers [72,74] could be obtained even if an excess of metal salt was used. This reactivity is further evidence that it is not steric factors that determine the nuclearity of complexes incorporating this type of potentially dinucleating ligand.

7. Summary

4-Substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles have been shown to be versatile ligands for a variety of transition metals. Coordination compounds with metal-to-ligand molar ratios of 1:1, 1:2, 2:1 and 2:2 have been obtained while other possible ratios, e.g. 1:3, have not been observed so far. Among the many different coordination modes featured in these complexes the mononuclear octahedral *trans*-$(N',N^1)_2$ coordination mode is by far the most common one. Dinuclear complexes are rare and have only been obtained with two of these ligands while attempts to prepare such complexes with other members of this ligand class either have not been carried out or have failed. This difference in reactivity is probably due to electronic rather than steric effects of the respective substituents on N^4. However, systematic studies investigating the influence of the choice of the metal, counterion and N^4 substituent on the coordination behaviour of these ligands remain to be undertaken. Interestingly, almost all complexes of 4-heteroaryl- and 4-aryl-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles, 2,5-di(2-pyridyl)-1,3,4-oxadiazole and 2,5-di(2-pyridyl)-1,3,4-thiadiazole have been structurally characterised while this is only the case for about a third of the complexes incorporating 4-amino-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole as a ligand. This may be an indication that substituents other than the 4-amino group positively

Table 4
Survey of complexes of 2,5-di(2-pyridyl)-1,3,4-oxadiazole (dpox, **XXIII**)

Complex	Description and remarks	CCDC code	Reference
$[Ni^{II}(dpox)_2(H_2O)_2](ClO_4)_2$ **(51)**	Octahedral, mononuclear *trans*-$(N',N^1)_2$ mode	FUHLAV	[73]
$[Cu^{II}(dpox)_2(H_2O)_2](ClO_4)_2$ **(52)**	Octahedral, mononuclear *trans*-$(N',N^1)_2$ mode	JEGLOW JEGLOW01	[71,74]
$[Cu^{II}(dpox)_2Cl_2]\cdot 2H_2O$ **(53)**	Octahedral, mononuclear *trans*-$(N',N^1)_2$ mode	KUJYET	[72]
$[Cu^{II}(dpox)Cl_2]_\infty$ **(54)**	Octahedral, one-dimensional polymer made up of metal ion linked *trans*-$(N',N^1)_2$ units, chlorides in axial positions	KUJYIX	[72]
$[Cu^{II}(dpox)_2(H_2O)_2](CF_3SO_3)_2$ **(55)**	Octahedral, mononuclear *trans*-$(N',N^1)_2$ mode	FUHHIZ	[73]
$[Cu^{II}(dpox)(NO_3)_2]_\infty$ **(56)**	Octahedral, one-dimensional polymer made up of metal ion linked *trans*-$(N',N^1)_2$ units, coordinating nitrates in axial positions	XILLIN	[74]
$[Pt^{II}(dpox)(CH_3)_2]$ **(57)**		–	[70]
$[Pt^{IV}(dpox)(CH_3)_3I]$ **(58)**		–	[70]

Table 5
Survey of complexes of 2,5-di(2-pyridyl)-1,3,4-thiadiazole (dptd, **XIV**)

Complex	Description and remarks	CCDC code	Reference
$[Co^{II}(dptd)_2(H_2O)_2](NO_3)_2$ **(59)**	Octahedral, mononuclear *trans*-$(N',N^1)_2$ mode	MINPAA	[75]
$[Co^{II}(dptd)_2(H_2O)_2](ClO_4)_2$ **(60)**	Octahedral, mononuclear *trans*-$(N',N^1)_2$ mode	MINPII	[75]
$[Ni^{II}(dptd)_2(H_2O)_2](ClO_4)_2$ **(61)**	Octahedral, mononuclear *trans*-$(N',N^1)_2$ mode	MINPEE	[75]
$[Cu^{II}(dptd)_2(NO_3)_2]$ **(62)**	Octahedral, mononuclear *trans*-$(N',N^1)_2$ mode, coordinating nitrates in axial positions	MINPOO	[75]

influence the crystallisation behaviour of the respective coordination compounds.

Acknowledgements

This work was supported by a University of Otago Postgraduate Scholarship to MHK. The authors thank Dr. U. Beckmann for helpful discussions.

References

[1] J.G. Haasnoot, Coord. Chem. Rev. 200–202 (2000) 131.
[2] J.F. Geldard, F. Lions, J. Org. Chem. 30 (1965) 318.
[3] F. Dallacker, Monatsh. Chem. 91 (1960) 294.
[4] A. Bencini, D. Gatteschi, C. Zanchini, J.G. Haasnoot, R. Prins, J. Reedijk, Inorg. Chem. 24 (1985) 2812.
[5] R. Prins, P.J.M.W.L. Birker, J.G. Haasnoot, G.C. Verschoor, J. Reedijk, Inorg. Chem. 24 (1985) 4128.
[6] F.J. Keij, R.A.G. de Graaff, J.G. Haasnoot, J. Reedijk, J. Chem. Soc. Dalton Trans. (1984) 2093.
[7] R. Hage, A.H.J. Dijkhuis, J.G. Haasnoot, R. Prins, J. Reedijk, B.E. Buchanan, J.G. Vos, Inorg. Chem. 27 (1988) 2185.
[8] R. Hage, J.G. Haasnoot, D.J. Stufkens, T.L. Snoeck, J.G. Vos, J. Reedijk, Inorg. Chem. 28 (1989) 1413.
[9] F. Barigellitti, L. De Cola, V. Balzani, R. Hage, J.G. Haasnoot, J. Reedijk, J.G. Vos, Inorg. Chem. 28 (1989) 4344.
[10] R. Hage, J.G. Haasnoot, H.A. Nieuwenhuis, J. Reedijk, D.J.A. De Ridder, J.G. Vos, J. Am. Chem. Soc. 112 (1990) 9245.
[11] F. Barigellitti, L. De Cola, V. Balzani, R. Hage, J.G. Haasnoot, J. Reedijk, J.G. Vos, Inorg. Chem. 30 (1991) 641.
[12] R. Hage, J.G. Haasnoot, J. Reedijk, R. Wang, J.G. Vos, Inorg. Chem. 30 (1991) 3263.
[13] L. De Cola, F. Barigellitti, V. Balzani, R. Hage, J.G. Haasnoot, J. Reedijk, J.G. Vos, Chem. Phys. Lett. 178 (1991) 491.
[14] J.H. van Diemen, R. Hage, J.G. Haasnoot, H.E.B. Lempers, J. Reedijk, J.G. Vos, L. De Cola, F. Barigellitti, V. Balzani, Inorg. Chem. 31 (1992) 3518.
[15] H.P. Hughes, D. Martin, S. Bell, J.J. McGarvey, J.G. Vos, Inorg. Chem. 32 (1993) 4402.
[16] S. Serroni, S. Campagna, G. Denti, T.E. Keyes, J.G. Vos, Inorg. Chem. 35 (1996) 4513.
[17] K.F. Mongey, J.G. Vos, B.D. MacCraith, C.M. McDonagh, Coord. Chem. Rev. 185–186 (1999) 417.
[18] F. Gasparrini, I. D'Acquarica, J.G. Vos, C.M. O'Connor, C. Villani, Tetrahedron: Asymmetry 11 (2000) 3535.
[19] A.C. Lees, C.J. Kleverlaan, C.A. Bignozzi, J.G. Vos, Inorg. Chem. 40 (2001) 5343.
[20] W.R. Browne, C.M. O'Connor, C. Villani, J.G. Vos, Inorg. Chem. 40 (2001) 5461.
[21] C. Di Pietro, S. Serroni, S. Campagna, M.T. Gandolfi, R. Ballardini, S. Fanni, W.R. Browne, J.G. Vos, Inorg. Chem. 41 (2002) 2871.
[22] J.-S. Wang, C.-F. Sheu, J.-S. Lee, Acta Crystallogr. Sect. C 55 (1999) 1806.
[23] N.-D. Sung, K.-S. Yun, J.-G. Kim, I.-H. Suh, Acta Crystallogr. Sect. C 56 (2000) e370.
[24] N.-D. Sung, K.-S. Yun, T.-Y. Kim, K.-Y. Choi, M. Suh, J.-G. Kim, I.-H. Suh, J. Chin, Inorg. Chem. Commun. 4 (2001) 377.
[25] C. Faulmann, P.J. van Koningsbruggen, R.A.G. de Graaff, J.G. Haasnoot, J. Reedijk, Acta Crystallogr. Sect. C 46 (1990) 2357.
[26] J.P. Cornelissen, J.H. van Diemen, L.R. Groeneveld, J.G. Haasnoot, A.L. Spek, J. Reedijk, Inorg. Chem. 31 (1992) 198.
[27] U. Hartmann, H. Vahrenkamp, Inorg. Chim. Acta 239 (1995) 13.
[28] P.J. Kunkeler, P.J. van Koningsbruggen, J.P. Cornelissen, A.N. van der Horst, A.M. van der Kraan, A.L. Spek, J.G. Haasnoot, J. Reedijk, J. Am. Chem. Soc. 118 (1996) 2190.
[29] A.J. Jircitano, S.O. Sommerer, K.A. Abboud, Acta Crystallogr. Sect. C 53 (1997) 434.
[30] N. Moliner, M.C. Munoz, P.J. van Koningsbruggen, J.A. Real, Inorg. Chim. Acta 274 (1998) 1.
[31] N. Moliner, A.B. Gaspar, M.C. Munoz, V. Niel, J. Cano, J.A. Real, Inorg. Chem. 40 (2001) 3986.
[32] N. Moliner, M.C. Munoz, S. Letard, J.-F. Letard, X. Solans, R. Burriel, M. Castro, O. Kahn, J.A. Real, Inorg. Chim. Acta 291 (1999) 279.
[33] J.-F. Letard, L. Capes, G. Chastanet, N. Moliner, S. Letard, J.-A. Real, O. Kahn, Chem. Phys. Lett. 313 (1999) 115.
[34] P.J. van Koningsbruggen, D. Gatteschi, R.A.G. de Graaff, J.G. Haasnoot, J. Reedijk, C. Zanchini, Inorg. Chem. 34 (1995) 5175.
[35] P.J. van Koningsbruggen, K. Goubitz, J.G. Haasnoot, J. Reedijk, Inorg. Chim. Acta 268 (1998) 37.
[36] M.P. Garcia, J.A. Manero, L.A. Oro, M.C. Apreda, F.H. Cano, C. Foces-Foces, J.G. Haasnoot, R. Prins, J. Reedijk, Inorg. Chim. Acta 122 (1986) 235.
[37] A.L. Rheingold, P. Saisuwan, N.C. Thomas, Inorg. Chim. Acta 214 (1993) 41.
[38] H.M. Burke, J.F. Gallagher, M.T. Indelli, F. Scandola, J.G. Vos, Eur. J. Inorg. Chem. (2002) 846.
[39] H.G.O. Becker, G. Görmar, H.-J. Timpe, J. Prakt. Chem. 312 (1970) 610.
[40] J.G. Vos, personal communication, February 2003.
[41] G. Giuffrida, V. Ricevuto, G. Guglielmo, S. Campagna, M. Ciano, Inorg. Chim. Acta 194 (1992) 23.
[42] G. Calogero, G. Giuffrida, S. Serroni, V. Ricevuto, S. Campagna, Inorg. Chem. 34 (1995) 541.
[43] G. Di Marco, M. Lanza, M. Pieruccini, S. Campagna, Adv. Mater. 8 (1996) 576.
[44] G. Di Marco, M. Lanza, A. Mamo, I. Stefio, C. Di Pietro, G. Romeo, S. Campagna, Anal. Chem. 70 (1998) 5019.
[45] S. Kubota, M. Uda, T. Nakagawa, J. Heterocycl. Chem. 12 (1975) 855.
[46] M. Uda, Y. Hisazumi, K. Sato, S. Kubota, Chem. Pharm. Bull. 24 (1976) 3103.
[47] H. Takalo, V.-M. Mukkala, L. Meriö, J.C. Rodriguez-Ubis, R. Sedano, O. Juanes, E. Brunet, Helv. Chim. Acta 80 (1997) 372.
[48] M. Santus, Acta Pol. Pharm. 33 (1976) 577.
[49] S.K. Mandal, H.J. Clase, J.N. Bridson, S. Ray, Inorg. Chim. Acta 209 (1993) 1.
[50] In the original communication, the authors stated they had used 2,5-dimethoxydihydrofuran for the introduction of the pyrrole ring in triazole **IX**. However, this must be an error as the standard reagent for this transformation is 2,5-dimethoxytetrahydrofuran [51].
[51] N. Elming, N. Clauson-Kaas, Acta Chem. Scand. 6 (1952) 867.
[52] Cambridge Crystallographic Data Centre, personal communication, November 2002.
[53] X. Ren, S.K. Mandal, P.G. Pickup, J. Electroanal. Chem. 389 (1995) 115.
[54] E. Klingsberg, J. Org. Chem. 23 (1958) 1086.
[55] D.-R. Zhu, Y. Xu, Y. Zhang, T.-W. Wang, X.-Z. You, Acta Crystallogr. Sect. C 56 (2000) 895.
[56] Z. Wang, Z. Bai, J. Yang, K. Okamoto, X. You, Acta Crystallogr. Sect. C 54 (1998) 438.
[57] W. Chen, Z.X. Wang, F.F. Jian, Z.P. Bai, X.Z. You, Acta Crystallogr. Sect. C 54 (1998) 851.
[58] H.-K. Fun, K. Chinnakali, S. Shao, D. Zhu, X.Z. You, Acta Crystallogr. Sect. C 55 (1999) 770.
[59] D. Zhu, Y. Song, Y. Liu, Y. Xu, Y. Zhang, X. You, Transition Met. Chem. 25 (2000) 589.

[60] D. Zhu, Y. Xu, Y. Mei, Y. Shi, C. Tu, X. You, J. Mol. Struct. 559 (2001) 119.
[61] S.-C. Shao, D.-R. Zhu, X.-H. Zhu, X.-Z. You, S.S.S. Raj, H.-K. Fun, Acta Crystallogr. Sect. C 55 (1999) 1412.
[62] S.C. Shao, D.R. Zhu, T.W. Wang, Y. Zhang, S.S.S. Raj, H.K. Fun, Chin. Chem. Lett. 11 (2000) 93.
[63] D.-R. Zhu, Y. Song, Y. Xu, Y. Zhang, S.S.S. Raj, H.-K. Fun, X.-Z. You, Polyhedron 19 (2000) 2019.
[64] D. Zhu, Y. Xu, Z. Yu, Z. Guo, H. Sang, T. Liu, X. You, Chem. Mater. 14 (2002) 838.
[65] B. Modzelewska-Banachiewcz, D. Matosiuk, Pharmazie 54 (1999) 588.
[66] S. Sueur, J.P. Wignacourt, G. Nowogrocki, M. Lagrenee, Acta Crystallogr. Sect. C 47 (1991) 1877.
[67] G. Giuffrida, G. Calogero, G. Guglielmo, V. Ricevuto, M. Ciano, S. Campagna, Inorg. Chem. 32 (1993) 1179.
[68] G. Giuffrida, G. Calogero, G. Guglielmo, V. Ricevuto, S. Campagna, Inorg. Chim. Acta 251 (1996) 255.
[69] G. Giuffrida, G. Calogero, V. Ricevuto, S. Campagna, Inorg. Chem. 34 (1995) 1957.
[70] J.D. Scott, R.J. Puddephatt, Organometallics 5 (1986) 2522.
[71] J.P. Wignacourt, S. Sueur, M. Lagrenee, Acta Crystallogr. Sect. C 46 (1990) 394.
[72] M. Lagrenee, S. Sueur, J.P. Wignacourt, B. Mernari, A. Boukhari, J. Chim. Phys. Phys.-Chim. Biol. 88 (1991) 2075.
[73] A. Gueddi, B. Mernari, M. Giorgi, M. Pierrot, Acta Crystallogr. Sect. C 56 (2000) e426.
[74] X.-H. Bu, H. Liu, M. Du, L. Zhang, Y.-M. Guo, M. Shionoya, J. Ribas, Inorg. Chem. 41 (2002) 1855.
[75] F. Bentiss, M. Lagrenee, J.P. Wignacourt, E.M. Holt, Polyhedron 21 (2002) 403.