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Mononuclear, oligonuclear and polynuclear metal coordination compounds with 1,2,4-triazole derivatives as ligands

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This paper is dedicated to the memory of Olivier Kahn

Contents

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Abstract

1,2,4-Triazole and its derivatives have gained great attention as ligands to transition metals by the fact that they unite the coordination geometry of both pyrazoles and imidazoles, and in addition exhibit a strong and typical property of acting as bridging ligands between two metal centres. In this bridging capacity, the 1,2,4-triazole ligands show a great coordination diversity, especially when the triazole nucleus is substituted with additional donor groups. This property together with their strong σ donor properties and the relative ease of synthesis make them very appealing for the design of new polynuclear metal complexes with interesting properties. A number of X-ray structures have been evaluated in some detail in the present paper.

Keywords: 1,2,4-Triazole derivatives; Metal complexes; Polynuclear transition metal compounds; X-ray structures; Spectroscopic and magnetic properties

1. Introduction

Although coordination compounds of 1,2,4-triazoles have been known for more than a century [1], the beginning of their systematic study, however, dates from the late 1970s. This is well after the first publications of crystal structures of the polynuclear $CuCl_2(Htrz)$ in 1961 [2] and the trinuclear $[Ni_3(Htrz)_6(H_2O)_6](NO_3)_6{\cdot}2H_2O$ in 1968 [3,4]. The chemistry of the triazole[1] complexes and the knowledge of their structures and properties however have increased rather quickly since the early 1980s. In a review on the organic chemistry of 1,2,4-triazoles in 1960 Potts [5] only noted the use of triazole complexes of silver for applications in the photographic industry, although quite a number of complexes with other metals had already been described at that time. Triazole complexes have been the subject of a chapter in a review up to the year 1974 by Temple [6]. However, not many compounds in this class had been described and very few crystal structures were known.

The number of reports on metal compounds with triazoles in the literature, including patents, is of the order of thousands, and rapidly growing. Close to 200 reports of (X-ray) structure determinations of triazole-metal complexes are known and this number is increasing quite fast. Table 1 surveys triazole complexes for which the X-ray single-crystal structure has been determined up until mid 1998. The structure of many more triazole complexes are known because of isomorphism or by determination by other methods.

Around the world many research groups investigate metal triazoles complexes, the main players in this field being Janiak, Berlin/Freiburg [7,8], Kahn, Bordeaux [9], Vos, Dublin [10], Salas, Granada [11], Haasnoot/Reedijk, Leiden [12], Robert, Mons [13], Lavrenova/Larionov, Novosibirsk [14], Goodwin, Sydney [15], Szłyk, Toruń [16], Varret, Versailles [17], Real, Valencia [275].

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[1] The word *triazole* without prefix locant numbers is used frequently throughout this paper to denote *1,2,4-triazole*.

Table 1
Complexes of 1,2,4-triazoles determined by X-ray crystallography

Compound	Description of structure	Ref.
$\mathrm{CuCl_2(Htrz)}$	Polynuclear chain with triple bridges of two chlorides and one N1*N*2 triazole	[2]
$\mathrm{[Ni_3(Htrz)_6(H_2O)_6](NO_3)_6{\cdot}2H_2O}$	Trinuclear, triple bridges of three triazoles	[3,4]
Ag(mtpo)	2D-Polynuclear, interconnected dimers	[197]
$\mathrm{Mn(Htrz)_2(NCS)_2}$	2D-Polynuclear, single bridges of *N*2*N*4 triazole	[57]
$\mathrm{Co(Htrz)_2(NCS)_2}$	2D-Polynuclear, single bridges of *N*2*N*4 triazole	[58,77]
$\mathrm{Cu(Htrz)_2(NCS)_2}$	2D-Polynuclear, single bridges of *N*2*N*4 triazole	[58]
$\mathrm{Zn(Htrz)_2(NCS)_2}$	2D-Polynuclear, single bridges of *N*2*N*4 triazole	[58]
$\mathrm{Mn_2(4Metrz)_5(NCS)_4}$	Dinuclear, triple triazole bridge, two monodentate triazoles	[59]
$\mathrm{Co_2(4Phtrz)_5(NCS)_4{\cdot}2.7H_2O}$	Dinuclear, triple triazole bridge	[61]
$\mathrm{Fe(Htrz)_2(NCS)_2}$	2D-Polynuclear, single bridges of *N*2*N*4 triazole	[65]
$\mathrm{[Mn(Htrz)(H_2O)_4SO_4]}$	Mononuclear, *N*4 coordinating triazole	[95]
$\mathrm{CuCl_2(1Ettrz)_2}$	Mononuclear *N*4-coordinating triazole, square-planar copper	[140]
$\mathrm{[Ni_2(4Ettrz)_4(H_2O)(NCS)_4]{\cdot}5/2H_2O}$	Asymmetric dinuclear, triple *N*1,*N*2 triazole bridge	[125]
$\mathrm{[CuCl_2(1\text{-}\beta\text{-}D\text{-}ribofuranosyl\text{-}3\text{-}carboxamide\text{-}trz)]}$	Mononuclear, distorted square-planar, *N*4,*O*(carboxamide) coordination	[201]
$\mathrm{Cr(CO)_5(4Metrz)}$	Mononuclear, *N*1-coordinating triazole	[122]
$\mathrm{[Cu_2(35Py_2trz)_2(NO_3)_2(H_2O)_2]{\cdot}1/2H_2O}$	Dinuclear, planar double *N*1*N*2 triazole bridge	[202,203]
$\mathrm{[Cd_2(NCS)_4(4^{\mathit{t}}Butrz)_3]_{\infty}}$	Chain with alternating bridges of three triazoles and two *N*-bonded thiocyanates	[131]
$\mathrm{[Zn(4^{\mathit{t}}Butrz)_2(NCS)_2]}$	Mononuclear, *N*1-coordinating triazole	[130]
$\mathrm{[Cd(dmtp)_2(H_2O)_2(NCS)_2]}$	mononuclear, two *N*3-dmtp *trans*	[185]
$\mathrm{[Hg(dmtp)_2(SCN)_2]}$	Mononuclear, tetrahedral, *S*-bonded thiocyanates	[185]
$\mathrm{\alpha\text{-}[\{Cu(dmtp)_2(NSC)\}_2(NCS)_2]}$	Dinuclear, double *N*,*S*-thiocyanate bridge, Cu in tetragonal pyramid, α has *S* apex, *N*3 dmtp	[189]
$\mathrm{\beta\text{-}[\{Cu(dmtp)_2(NSC)\}_2(NCS)_2]}$	Dinuclear, double *N*,*S*-thiocyanate bridge, Cu in tetragonal pyramid, β has *S* equatorial, *N*3 dmtp	[204]
$\mathrm{[Pt(dmtp)_4][Pt(SCN)_6]}$	Ionic $\mathrm{Pt^{2+}}$–$\mathrm{Pt^{4+}}$ compound, $\mathrm{Pt^{2+}}$ square-planar, dmtp-*N*3, *S*-bonded thiocyanates	[189]
$\mathrm{[Fe_3(4Ettrz)_6(H_2O)_6](CF_3SO_3)_6}$	Trinuclear with two triple *N*1,*N*2 triazole bridges	[128,26]
$\mathrm{[Zn_3(4Ettrz)_6(H_2O)_6](CF_3SO_3)_6}$	Linear trinuclear with two triple *N*1,*N*2 triazole bridges	[205]
$\mathrm{Cd(Htrz)_2(NCS)_2}$	Polynuclear chain with double *N*,*S*-thiocyanate bridges, *N*4 triazole	[96]

Table 1 (Continued)

Compound	Description of structure	Ref.
$[Fe(bpy)(Htrz)Cl_3]$	Mononuclear, *fac*-trichloro, *N*4-triazole	[97]
$[Ni_3(35Et_2Htrz)_6(NCS)_6]\cdot 2H_2O$	Trinuclear with two bridges of two *N*1,*N*2-triazoles and one *N*-bridging thiocyanate	[30]
$[Co(dmtp)_3(H_2O)(NCS)_2Hg(SCN)_2]_2$	Cyclic Co,Hg alternating tetranuclear with single *N*,*S*-thiocyanate bridges, dmtp *N*3	[186]
$[Ni_2(35Py_24atrz)_2Cl_2(H_2O)_2]Cl_2\cdot 4H_2O$	Dinuclear with planar double *N*1,*N*2-triazole bridge	[155]
$[Rh_3(trz)(Cl)Cl(tfb)(CO)_4]\cdot 1/2CH_2Cl_2$	Stacks of trinuclears, triazolate bridging between three rhodium atoms	[40]
$[Rh_3(trz)(Cl)Cl(C_3H_5)(CO)_4]\cdot 1/2C_2H_4Cl_2$	Chain of trinuclears, triazolate between three rhodium atoms	[40]
$Fe_2Hg_2(dmtp)_4(NCS)_8(H_2O)_3$	Chains of Fe_4Hg_4 alternating cycles formed by $Hg(SCN)_4$ units linking iron centers, *N*3 dmtp	[187]
$Fe_2Hg_2(dmtp)_4(NCS)_8(H_2O)_2$	Three-dimensional network of iron centers linked by $Hg(SCN)_4$ units	[187]
$Fe_2Hg_2(dmtp)_2(NCS)_8(H_2O)_4\cdot$acetone	Layers of iron centers linked by $Hg(SCN)_4$ units	[187]
$[(Cu_2L)_2(35Me_2trz)_2Cu](ClO_4)_3\cdot L =$ macrocyclic ligand	Pentanuclear complex, containing two- and three-coordinate Cu(I) linked via triply bridging dimethyltriazolates	[177]
$[Co_3(4^tButrz)_8(NCS)_4](NCS)_2\cdot 9H_2O$	Trinuclear, two triple *N*1,*N*2 triazole bridges, two triazoles *N*1 monodentate	[206]
$[Co_2(4Altrz)_4(H_2O)(NCS)_4]\cdot 2H_2O$	Asymmetric dinuclear, triple *N*1,*N*2 triazole bridge, one allyltriazole *N*1 monodentate	[207]
$[(\eta^3\text{-}C_3H_5)_2Pd_2(\mu^3\text{-}trz)Rh_2Cl_2(CO)_4]$	Tetranuclear, two triazolates bridge two Pd atoms via *N*1,*N*2; *N*4 atoms bound to $RhCl(CO)_2$ units	[41]
$[K(M)]NCS\cdot CH_3OH$M=18-crown-6 derivative in which one oxygen is replaced by *N*4 of 1-benzyl-triazole-3,5-dicarboxylic ester	Mononuclear potassium complex; complex group KO_5N, triazole *N*4 donor	[208]
$[Co_3(35Et_2Htrz)_6F_2(NCS)_4]\cdot 2H_2O$	Trinuclear with two bridges each consisting of one fluoride and two *N*1,*N*2 triazoles, two triazoles *N*1 monodentate	[28]
$[Mn_3(4Ettrz)_6(H_2O)_6](CF_3SO_3)_6$	Trinuclear with two triple *N*1,*N*2 triazole bridges	[209]
$[Cu_2(35Py_2trz)_2(CF_3SO_3)_2(H_2O)_2]$	Dinuclear, planar double *N*1,*N*2 bridge of dipyridyltriazoles	[203,210]
$[Co(btr)_2(NCS)_2]\cdot H_2O$	Quadratic layers of Co(II) bridged by *N*1,*N*1′ coordinating btr	[111]
$[CuHg(dmtp)_2(SCN)_3]$	Polynuclear layers of alternating Cu(I) and Hg(II), each with one *N*3 dmtp ligand, thiocyanates bridge *N* to Cu and *S* to Hg	[188]
$[Rh_3(trz)Cl_2(\eta^4\text{-}tfb)(CO)_4]\cdot 1/2CH_2Cl_2$	Stacks of trinuclear Rh_3 with μ^3 triazolate	[23]
$[Co_3(345Me_3trz)_4F_2(NCS)_4(H_2O)_2]\cdot 4H_2O$	Trinuclear two triple bridges each consisting of one fluoride and two *N*1,*N*2 triazoles	[29]
$[Cu(dmtp)_4(H_2O)_2](PF_6)_2$	Mononuclear, H_2O ligands *trans*, *N*3 dmtp	[194]
$[Rh_3(trz)_3(\eta^3C_3H_5)_6]$	Triangular arrangement of three $Rh(C_3H_5)_2$ moieties, connected by three *N*1,*N*4 bridging triazoles	[42]

Table 1 (Continued)

Compound	Description of structure	Ref.
$[Rh_3(trz)Cl_2(C_3H_5)_2(CO)_4]\cdot 1/2C_2H_4Cl_2$	Trinuclear with μ^3 bridging tridentate triazolate, one additional chloride bridge between two Rh atoms	[42]
$[Fe(5mtp)_2(H_2O)_2(NCS)_2]$	Mononuclear, two 5mtp ligands *N*3 *trans*	[182]
$[Co(5mtp)_2(H_2O)_2(NCS)_2]$	Mononuclear, two 5mtp ligands *N*3 *trans*	[183]
$[Zn(tp)_2Br_2]\cdot 1/2H_2O$	Mononuclear, pseudo tetrahedral, tp *N*3	[179]
$[Cd(dmtpz)_2(NCS)_2]$	One-dimensional chain of Cd, linked by double NCS bridges, dmptz *N*2	[200]
$[Cu_4(ppt)(H_2O)]_4(NO_3)_4\cdot 12H_2O$	Tetrahedral tetranuclear, ppt ligands *N*1,*N*2 bridging pairs of copper(II)	[159]
$[Rh(CO)_2(35Py_24atrz)]ClO_4$	Mononuclear, Rh square-planar coordinated by two CO and one *N*1,*N*1′ chelating aminodipyridyltriazole	[92]
$[Fe(tp)_2(NCS)_2]$	Two-dimensional arrays of iron atoms connected by *N*1,*N*3 coordinating triazolopyrimidine ligands	[36]
$[Cu(tp)_2NCS)_2]$	Two-dimensional arrays of Cu^{2+} atoms connected by *N*1,*N*3 tp, *N*1 in semi-coordination	[181]
$[Cu(tp)_2Cl_2]$	Two-dimensional arrays of Cu^{2+} atoms connected by *N*1,*N*3 tp, *N*1 in semi-coordination	[181]
$Ni_8(NCS)_8(ahmt)(Hahmt)_4(H_2ahmt)_4(H_2O)_{12}$	Octanuclear; two cubane-type Ni_4O_4 clusters connected through the dianionic amino-bishydroxymethyltriazole	[172]
$[Co(btr)_3](CF_3SO_3)_2$	3d Network of *N*1,*N*1′ coordinating btr	[120]
$[Cu(4atrz)_3](ClO_4)_2\cdot 1/2H_2O$	Polynuclear chain, triple *N*1,*N*2 triazole bridges	[211]
$[Cu(mtpo)_2(NH_3)_2(H_2O)_2]$	Mononuclear, all *trans*, *N*3 mtpo	[198]
$[Cu(mtpo)_2(H_2O)_4]$	Mononuclear, all *trans*, *N*3 mtpo	[198]
$Co_6(3Me4Ettrz)_{14}(H_2O)_{18}(CF_3SO_3)_{12}$	Two different trinuclear cations, triple triazole *N*1,*N*2 bridges	[212]
$[Cu(4atrz)_4(H_2O)](ClO_4)_2$	Mononuclear, *N*1 coordination	[213]
$[Cu_3(OH)(hppt)_3](NO_3)_2\cdot 4H_2O$	μ^3-Hydroxy bridged triangle of three Cu^{2+} ions, edges bridged by *N*1,*N*2 triazoles chelating with phenolato-*O*	[120]
$[Ag_3(M)(NO_3)_2]_\infty$ M = 18-crown-6 derivative in which one oxygen is replaced by *N*4 of triazolate anion	Chain through *N*1,*N*4 of trinuclear complex, trz coordinates with *N*1, *N*2 and *N*4 to three different silver ions	[214]
$[Mn(btr)_2(H_2O)_2](NO_3)_2\cdot 2H_2O$	Two-dimensional quadratic array *N*1,*N*1′ bridging btr ligands	[119]
$[Ru(1Me3Pytrz)(CH_3CN)Cl_3]$	*mer*-Trichloro, *N*2,*N*1′ chelate	[215]
$[(CH_3)_2Tl(3CF_35S4atrz)]$	*N*1,*S* Coordinating ligands link dimethyl-thallium moieties to chains, chains are paired by additional semi-coordination of *S*	[216]

Table 1 (Continued)

Compound	Description of structure	Ref.
$[Cu_4(dmtp)_4Cl_2][Cu_2Cl_4]$	Tetranuclear cations of two pairs of Cu(I) atoms connected by double *N*3,*N*4 dmtp bridges, chlorides bridge between pairs	[191]
$[CdL_2Cl_2]$ L = 8-chloro-6-(*o*-chlorophenyl) -1-methyl-4H-s-triazolo(4,3-*a*)1,4-benzodiazepine	Cd tetrahedrally coordinated by two Cl and two triazole *N*1	[217]
$[Cu_2(aamt)_2Br_2(H_2O)_2]Br_2{\cdot}2H_2O{\cdot}CH_3OH$	Dinuclear, planar double *N*1,*N*2 bridge, bis-chelate	[218]
$[Cu(aat)_2(H_2O)_2]SO_4{\cdot}5H_2O$	Mononuclear, all *trans*, two *N*4,O chelates	[219]
$[Ru(bpy)_2(35Py_2trz)]PF_6{\cdot}1/2H_2O$	Mononuclear, *N*2,*N*1′ chelate	[220]
$[Ru(bpy)_2(4Altrz)_2](PF_6)_2$	Mononuclear, *N*1 monodentate triazoles	[221]
$[Ni(dmtp)_2(H_2O)_4]I_2{\cdot}2H_2O$	Mononuclear, dmtp *N*3	[222]
$[Ni(dmtp)_4(H_2O)_2](I_3)_2{\cdot}2dmtp$	Mononuclear, dmtp *N*3	[222]
$[Cu(6mtp)_2(NCS)_2]$	Mononuclear, square planar copper, *trans*, *N*3 6mtp	[184]
$[Cu(5mtp)_2(NCS)_2]$	Pseudo 2-d layer, *N*1,*N*3 bridges of 5mtp, *N*1 semi-coordination	[184]
$[Ru(1Me3Pytrz)_2(CO)Cl]PF_6$	Mononuclear, two *N*4,*N*1′ chelates	[223]
$[Ni_3(35a_2trz)_6(NCS)_6]{\cdot}6H_2O$	Trinuclear, two triple *N*1,*N*2 guanazole bridges	[139]
$[Cu(3Me4atrz)Cl_2]$	Polynuclear chain with triple bridges of two chlorides and one *N*1*N*2 triazole	[224]
$[Cu_3(3Me4Ettrz)(H_2O)_4](CF_3SO_3)_6{\cdot}5H_2O$	Trinuclear, two triple *N*1,*N*2 bridges	[134]
$[Ru(bpy)_2(H_2ppyt)]PF_6{\cdot}$acetone	Mononuclear, *N*1,*N*1′ chelate, strong hydrogen bond between *N*4 and phenolic *O*	[225]
$[Ru(bpy)_2(3Me5Pytrz)]PF_6{\cdot}4H_2O$	Mononuclear, *N*1,*N*1′ chelate	[162]
$[Pd(dmtp)_2Br_2]{\cdot}CH_3OH$	Mononuclear, *trans* square-planar, dmtp *N*3	[226]
$[Mn(35Py_24atrz)_2(H_2O)_2]Br_2$	Mononuclear, all *trans*, *N*1,*N*1′ chelate	[157]
$[Ru(bpy)_2(35Py_2trz)Ru(bpy)_2](CF_3SO_3)_3{\cdot}4H_2O$	dinuclear, *N*1,*N*1′ and *N*4,*N*1″ chelate bridge	[37]
$[Ru(bpy)_2(35Py_2trz)Os(bpy)_2](CF_3SO_3)_3{\cdot}4H_2O$	Dinuclear, *N*1,*N*1′ and *N*4,*N*1″ chelate bridge resp. to Ru and Os	[37]
$[Cd(35a_2trz)_2(NCS)_2]$	2-Dimensional, *N*2,*N*4 bridges	[35]
$[Fe(btr)_2(NCS)_2]{\cdot}H_2O$	Quadratic layers of Fe(II) bridged by *N*1,*N*1′ coordinating btr	[113]
$[W(CO)_5(3Me1Pytrz)]$	Mononuclear, *N*4 monodentate ligand	[227]
$[Ir(ppy)_2(4Me3Pytrz)]PF_6$	Mononuclear, *N*2,*N*1′ chelate	[228]
$[Rh(ppy)_2(3Ph5Pytrz)]PF_6{\cdot}CH_3COCH_3$	Mononuclear, *N*4,*N*1′ chelate	[229]
$[Co(NH_3)_5(4atrz)](C(NO_2)_3)_3$	Mononuclear, *N*1 coordination	[230]
$[Pd_3(35a_2trz)_4Cl_4]Cl_2{\cdot}2H_2O$	Cyclic trinuclear, one double *N*1,*N*2 and two single *N*1,*N*2 bridges, Pd square-planar	[231]

Table 1 (Continued)

Compound	Description of structure	Ref.
$[Cu(tp)_2(H_2O)Br_2]$	Mononuclear, trigonal bipyramidal, *N*3 tp ligands *trans*	[232]
$[Fe(btr)_2(NCSe)_2]\cdot H_2O$	Quadratic layers of Fe(II) bridged by *N*1,*N*1′ coordinating btr	[114]
$[Ag_2(Htrz)_2(NO_3)_2]$	Dinuclear, planar double *N*1,*N*2 bridge	[82]
$[Co_3(35a_2trz)_2(35a_2Htrz)_4(H_2O)_6]Cl_3\cdot 9H_2O$	Trinuclear, two triple *N*1,*N*2 bridges	[27]
$[Pt(35a_2H_2trz)_2Br_2]Br_2$	Mononuclear, diaminotriazolium ligands coordinating through *N*1, *trans*	[233]
$[Cu(35Py_24atrz)_2(TCNQ)_2]$	Mononuclear, all *trans*, *N*1,*N*1′ chelate, stacked into chains by dimerized TCNQs	[234]
$[Ru(bpy)_2(3Me1Pytrz)Cl]PF_6$	Mononuclear, *N*4 coordination	[235]
$[Zn(35Me_24atrz)_2Cl_4]$	Dinuclear, planar double *N*1,*N*2 bridge	[236]
$[Cu_2(aamt)_2(H_2O)_2](SO_4)_2\cdot 4H_2O$	Dinuclear, planar double *N*1,*N*2 bridge double chelate	[237]
$[Cu(aat)_2(NCS)_2]$	Mononuclear, all *trans*, *N*1,*O* chelate, thiocyanate *N*-bonded	[175]
$[Cu(aat)_2(NCS)_2]$	Mononuclear, all *trans*, *N*1,*O* chelate, thiocyanate *S*-bonded	[175]
$[Cu(3Me_5SH_4atrz)Cl_2]\cdot H_2O$	Mononuclear, *S*,*N*(amino) chelate, square-planar copper(II)	[154]
$[Cu_2(3Me_5SH_4atrz)Cl_4]\cdot H_2O$	Polynuclear, *S*,*N*(amino) chelate combined with *N*1 coordination to second copper, dimers linked by double chloride bridges	[154]
$[Cu_3(3Me5SH4atrz)_2(H_2O)Cl_5]\cdot 2H_2O$	Trinuclear complex of two Cu(II) and one Cu(I), ligand involved in *N*1 coordination and *S*,*N*(amino) chelate	[154]
$[Co(dmtp)_2(H_2O)_4](NO_3)_2$	Mononuclear, *trans* *N*3 dmtp	[238]
$[Cd(dmtp)_2(H_2O)_4](NO_3)_2$	Mononuclear, *trans* *N*3 dmtp	[238]
$[Pd_3(35a_2trz)_4Br_4]Br_2\cdot 2H_2O$	Cyclic trinuclear, one double *N*1,*N*2 and two single *N*1,*N*2 bridges, Pd square-planar	[239]
$[Mn(35a_2Htrz)_2(NCS)_2]$	2-d Quadratic layer structure, *N*2,*N*4 bridges	[34]
$[Co(aat)_2(H_2O)_2]Br_2$	Mononuclear, *N*4,*O* chelate aat, all *trans*	[176]
$[Cu3(tdca)_2(dien)(H_2O)_2]\cdot 3H_2O$	Chain of asymmetric trinuclear sub-structures, ligand: *N*1,*N*2 bridge and *N*1,*O* and *N*4,*O*′ double chelate	[173]
$[Co_2(dppt)_2(H_2O)_4]Cl_4\cdot 2CH_3OH\cdot 2H_2O$	Dinuclear, planar double *N*1,*N*2 bridge, bis-*N*,*N*′-chelate	[240]
$[Cu_3(H_2ahmt)_6Cl_4]Cl_2$	Linear trinuclear, bridges consist each of one chloride and two *N*1,*N*2 triazoles, two ligands *N*1 monodentate	[241]
$[Cu_2(3Pytrz)_2(1Meiz)_2(H_2O)_2(NO_3)_2]\cdot 4H_2O$	Dinuclear, planar double *N*1,*N*2 triazole bridge, *N*2,*N*1′ chelate, methylimidazole monodentate	[163]
$[Cu_2(3Pytrz)_2(Hpz)_2(H_2O)_2(NO_3)_2]$	Dinuclear, planar double *N*1,*N*2 triazole bridge, *N*2,*N*1′ chelate, pyrazole monodentate	[163]
$[Cu_2(3Pytrz)_2(4,4'\text{-}bpy)(H_2O)_2(NO_3)](NO_3)\cdot 4H_2O$	Dinuclear, planar double *N*1,*N*2 triazole bridge, *N*2,*N*1′ chelate, 4,4′-bpy link dinuclear moieties to chain	[163]

Table 1 (Continued)

Compound	Description of structure	Ref.
HCA II 1,2,4-triazole complex HCA II = human carbonic anhydrase isoenzyme II	Zinc in tetrahedral coordination, triazole monodentate *N*4	[98]
$[Fe(btpy)_2](NO_3)_2 \cdot 4H_2O$	Mononuclear, *N*4,*N*′,*N*4′ chelate	[168]
$[Ni(btpy)_2]Cl_2 \cdot 3H_2O$	mononuclear, *N*4,*N*′,*N*4′ chelate	[168]
$[Ru(35Py_24atrz)(CO)_2Cl_2]$	Mononuclear, *N*1,*N*1′ chelate, chlorides *trans*	[242]
$[Cu(dmtp)_3(H_2O)_2](ClO_4)_2 \cdot 2H_2O$	Mononuclear, *mer* tris *N*3 dmtp, sixth water ligand in semi-coordination	[243]
$[Co(dmtp)_2(H_2O)_4]Br_2 \cdot H_2O$	Mononuclear, *N*3 dmtp	[244]
$[HB(trz)_3Mo(CO)_3]N(PPh_3)_2$	Mononuclear, *N*2 coordination	[245]
$[HB(trz)_3Mo(CO)_2(Et_2NCS_2)]$	Mononuclear, *N*2 coordination, $MoN_3C_2S_2$ chromophore	[145]
$[Cp_2Co][HB(35Me_2trz)_3MoO_2(SPh)] \cdot$toluene	*N*2 coordination, MoN_3O_2S chromophore	[146,246]
$[HB(35Me_2trz)_3MoO_2(SPh)]$	*N*2 coordination, MoN_3O_2S chromophore	[146,247]
$[HB(trz)_3Ru(CO)_2]_2 \cdot CH_2Cl_2$	Dinuclear, Ru–Ru, *N*2 coordination	[248]
$[Cu_2(3Pytrz)_2(H_2O)_3SO_4] \cdot 3H_2O$	Asymmetric dinuclear, planar double *N*1,*N*2 bridge, dimers stacked into pairs	[164]
$[Fe_3(4Me_2Ntrz)_6(H_2O)_6](ClO_4)_6 \cdot 2H_2O$	Trinuclear, two triple *N*1,*N*2 bridges	[107]
$[Cu_2Br_4(dmtp)_4] \cdot 2H_2O$	Dinuclear, double bromide bridge, *N*3 dmtp	[249]
$[Zn(dmtp)_2Cl_2]$	Mononuclear tetrahedral, *N*3 dmtp	[250]
$[Fe(HB(trz)_3)_2] \cdot 6H_2O$	Mononuclear, *N*2 coordination, hydrogen bonding to water molecules in layers	[19]
$[Co(HB(trz)_3)_2] \cdot 6H_2O$	Mononuclear, *N*2 coordination, hydrogen bonding to water molecules in layers	[19]
$[Cu(HB(trz)_3)_2] \cdot 4CH_3OH$	Mononuclear, *N*2 coordination, Jahn–Teller distortion	[149]
$[K(HB(trz)_3)_2] \cdot 2H_2O$	1d chain structure, K^+ bridged by disordered anionic ligands and water molecules	[149]
$[Zn(HB(trz)_3)_2] \cdot 6H_2O$	Mononuclear, *N*2 coordination, hydrogen bonding to water molecules in layers	[150]
$[Zn(HB(trz)_3)_2] \cdot \sim 1.5H_2O$	3d coordination polymer involving *N*4	[150]
$[Fe_3(^pCH_3Otrz)_8(H_2O)_4](BF_4)_6 \cdot 2H_2O$	Linear trinuclear, two triple *N*1,*N*2 bridges, two ligands *N*1 monodentate	[129]
$[Fe_3(^pCH_3Otrz)_6(H_2O)_6](BF_4)_6 \cdot 2CH_3OH \cdot 8H_2O$	Linear trinuclear, two triple *N*1,*N*2 bridges	[129]
$[Mn(btr)(H_2O)_2(NCS)_2]$	Polymeric chain, *N*1,*N*1′ bridges, all *trans* coordination	[118]
$[Cu_2(dien)_2Hdabt](ClO_4)_3$	Dinuclear, ligand constitutes planar double *N*2,*N*4 bridge, *N*1-hydrogen delocalized	[251]
$[Zn(trz)Cl]$	Layered polymer, triazolate *N*1,*N*2,*N*4 bridging	[39]

Table 1 (Continued)

Compound	Description of structure	Ref.
$[Fe(15Me_23Pytrz)_3](BF_4)_2$	Mononuclear, tris $N4,N1'$ chelate, *mer* isomer	[169]
$[Mn(H_2O)_2(H_2B(trz)_2)_2]\cdot 4H_2O$	2d coordination polymer, $N4,N4'$ bridges	[147]
$[Cu(H_2O)_2(H_2B(trz)_2)_2]\cdot 6H_2O$	1d coordination polymer, double $N4,N4'$ bridges	[147]
$[Ni(HB(trz)_3)_2]\cdot 6H_2O$	Mononuclear, $N2$ coordination, hydrogen bonding to water molecules in layers	[147]
$[Cu_2(35Py_24atrz)(H_2O)_4(SO_4)_2]\cdot H_2O$	Asymmetric dinuclear, bridge of O,O’ sulfate and $N1,N2$ triazole, one sulfate monodentate	[156]
$[Zn(35Py_24atrz)_2(H_2O)_2](ClO_4)_2$	Mononuclear, $N1,N1'$ chelate	[252]
$[Mn(H_2O)_2(HB(trz)_3)_2]\cdot 4H_2O$	1d chain structure, double $N4,N4'$ bridges	[153]
$[Ni(H_2O)_2(H_2B(trz)_2)_2]\cdot 2H_2O$	Mononuclear, $N2$ coordination	[153]
$[Cu(3Me5S4atrzH)]Cl$	Chain of Cu(I) chelated by amino group and S, linked to next ligand through $N2$	[253]
$[Ag_2(dmtp)_2(NO_3)_2]$	Dinuclear, double $N3,N4$ dmtp bridge	[192]
$[Cu(4Me3Nittrz)_4](ClO_4)_2$	Mononuclear, two ligands $N1$ coordination, two ligands $N1,O$ chelate	[174]
$[Fe(dmtph)_2](ClO_4)_2\cdot 0.67H_2O$	Mononuclear, $N4,N',N''$ chelate	[170]
$[Fe(dmtph)_2](ClO_4)_2\cdot H_2O$	Mononuclear, $N4,N',N''$ chelate	[170]
$[Cu(bmptb)]ClO_4\cdot CH_3CN$	Mononuclear, pseudotetrahedral, bis $N4,N'$ chelate	[171]
$[Cu(bmptb)](ClO_4)_2\cdot CH_3CN$	mononuclear, flattened tetrahedral, bis $N4,N'$ chelate	[171]
$[Fe(35Py_24atrz)_2(TCNQ)_2]$ structure determined at 298 and 100 K	Mononuclear, all *trans*, $N1,N1'$ chelate, stacked into chains by dimerized TCNQs	[158]
$[Cd(dmtp)(H_2O)_2SO_4]$	2d polynuclear, $N3$ dmtp, arranged into layers by sulfate linking three cadmium atoms	[195]
$[Fe(1mtph)_2](ClO_4)_2\cdot H_2O\cdot C_2H_5OH$	Mononuclear, $N4,N',N''$ chelate	[15]
$[Fe(5mtph)_2](ClO_4)_2\cdot 3H_2O$	Mononuclear, $N4,N',N''$ chelate	[15]
$[Cu_3(attn)_2(H_2O)_2Cl_2]Cl_4\cdot 4H_2O$	Linear trinuclear, each bridge consisting of one chloride and two $N1,N2$ triazoles	[137]
$[Cu_3(attn)_2(ZnCl_4)_2Cl_2]Cl_4\cdot 4H_2O$	Linear trinuclear in copper(II), each bridge consisting of one chloride and two $N1,N2$ triazoles, $ZnCl_4$ monodentate to copper	[137]
$[Ni_3(35a_2trz)_6(H_2O)_6](NO_3)_6\cdot 3H_2O$	Trinuclear, two triple $N1,N2$ bridges	[254]
$[Ni_3(3atrz)_6(H_2O)_6](NO_3)_6\cdot H_2O$	Trinuclear, two triple $N1,N2$ bridges	[255]
$[Ni_3(35a_2trz)_6(H_2O)_6](ClO_4)_6\cdot H_2O$	Trinuclear, two triple $N1,N2$ bridges	[256]
$(Et_4N)[HB(35Me_2trz)_3Mo(CO)_3]$	Mononuclear, $N2$ coordination	[257]
$[Ag(HB(trz)_3]$	Layered polynuclear, silver coordinated by two $N2$ and two $N4$	[152]
$[Hg(dmtp)_2Cl_2]$	Mononuclear, tetrahedral, $N3$ coordination	[258]
$[Zn(dmtp)_2Br_2]$	Mononuclear, tetrahedral, $N3$ coordination	[258]
$[Ag_2(dmtp)_2(HSO_4)_2]\cdot 4H_2O$	Dinuclear, centrosymmetric, double $N3,N4$ dmtp bridge	[193]

Table 1 (Continued)

Compound	Description of structure	Ref.
$[Ag_2(dmtp)_2SO_4][Ag(dmtp)_2Ag(HSO_4)_2]\cdot H_2O$	Two different ‘dimers’, the first developed to a polynuclear chain by linking sulfates, the second one has one Ag coordinated by two *N*3s and the other two *N*4 and two HSO_4	[193]
$[Pt_2(mtpo)_4]\cdot 2DMSO$	Dinuclear, quadruple *N*3,*N*4 mtpo bridge	[259]
$[Cu_2Cl_2(HB(trz)_3)_2]\cdot 2H_2O$	2d double layer polymer, *N*2 and *N*4 coordination	[151]
$[Cu_2(OH)_2(HB(trz)_3)]Cl\cdot 6H_2O$	3d polymer, *N*2 and *N*4 coordination, double OH bridges	[151]
$[Cu(satz)_2]\cdot 6H_2O$	Mononuclear, donor atoms phenoxy-*O* and azomethane-*N*	[260]
$[Cu(35Py_24atrz)_2(BF_4)_2]$	Mononuclear, *N*1,*N*1′ bridge, BF_4s axial	[261]
$[Cu(4atrz)Cl_2]$	1d polynuclear, bridges consist of two chlorides and one *N*1,*N*2 triazole	[106]
$[Cu(batt)Cl]\cdot H_2O$	Stacked to chain, ligand coordinates through *N*4,*N*′,*N*4′ chelate, chloride bridges	[13]
$[Pt(NH_3)_2(Hmtpo)_2](NO_3)_2\cdot 2H_2O$	Mononuclear, *cis*, *N*3 Hmtpo	[262]
$[Pt(NH_3)_2(mtpo)_2Pd(bpy)](NO_3)_2$	Heterodinuclear, square-planar metals bridged by two mtpo, Pt two *N*3, Pd two *N*4	[262]
$[(mtpo)Pt(NH_3)_2(mtpo)Pt(bpy)(OH)]NO_3\cdot 6H_2O$	Dinuclear, one mtpo *N*3 monodentate, one mtpo *N*3,*N*4 bridging, monodentate OH stabilised by hydrogen bonding	[262]
$[Cu_2(maamt)_2(CuCl_3)_2]$	Dinuclear in Cu(II), bridge consists of planar double chelating *N*1,*N*2 triazole and two stacking bridging $CuCl_3^{2-}$ anions	[165]
$[Pd_2(mtpo)_2(en)_2](NO_3)_2\cdot 2H_2O$	Dinuclear, double *cis* *N*3,*N*4 bridge, on each Pd en chelate	[263]
$[Pd_2(mtpo)_2(bpy)_2](NO_3)_2\cdot 5H_2O$	Dinuclear, double *cis* *N*3,*N*4 bridge, on each Pd bpy chelate	[263]
$[Fe_3(4^iPrtrz)_6(H_2O)_6](tosylate)_6\cdot 2H_2O$	Linear trinuclear, two triple *N*1,*N*2 bridges	[12]
$[Zn(dptp)_2Cl_2]$	Mononuclear, tetrahedral, *N*3 dptp	[16]
$[Co(dptp)_2Cl_2]$	Mononuclear, tetrahedral, *N*3 dptp	[16]
$[Hg(Hmpto)Cl_2]_2\cdot Hmpto\cdot H_2O$	Two independent mononuclear $HgCl_2$(Hmtpo) entities, bridged through chloride to double stacks, *N*1 Hmtpo	[178]
$[Cu_2(Hmtpo)_2(NCS)_4(H_2O)_2]$	Dinuclear, double *N*,*S* thiocyanate bridge, *N*3 Hmtpo	[264]
$[Ag(Hmtpo)NO_3]$	1d polymer, Hmtpo chelates to one silver atom through *N*1,*O* and bridges via *N*3	[11]
$[Ag(Hmtpo)(PPh_3)ClO_4]$	Chains with *N*1,*N*3 bridging Hmtpo, distorted tetrahedral N_2OP coordination	[11]
$[Ag_3(mtpo)_2(HSO_4)(H_2O)_2]\cdot H_2O$	Chains of trinuclear entities, *N*1,*O* chelate to one silver, bridging via *N*3 and *N*4 to two other ones	[11]
$[Cu(en)_2(mtpo)_2]$	Mononuclear, two *trans* *N*3 mtpo	[265]
$[Cu(4HOEttrz)_3](ClO_4)_2\cdot 3H_2O$	Linear chain of triple *N*1,*N*2 triazole bridges	[132]
$[Cu(dmtb)_4](ClO_4)_2$	Mononuclear, *N*4 coordination	[266]

Table 1 (Continued)

Compound	Description of structure	Ref.
$[Zn(dmtb)_6](ClO_4)_2$	Mononuclear, *N*4 coordination	[267]
$[Cu_2(tbima)_2(5S4atrz)](NO_3)_3]\cdot H_2O\cdot EtOH$	Dinuclear, 5S4atrz bridging through *N*1 and the 4-amino,5-thione chelate to two Cu(tbima) moieties	[268]
$[((MeNH_2)_2Pt(1\text{-}Me\text{-}cytosinato)_2Pd)_2(trz)](NO_3)_3$	*N*1,*N*4 triazolate is single bridge between Pds of two PtPd complexes, cytosine rings bridge through *N*3 and amino group	[94]
$(H_3O)[Cu_3(35Me_24atrz)_3(OH)Cl_6]$	Cyclic trinuclear, *N*1,*N*2 bridges, OH central	[138]
$[Zn(1\text{-}pinacolyl\text{-}trz)_6](ClO_4)_2$ pinacolyl = ^{t}Bu–C(O)–CH_2–	Mononuclear, *N*4 coordination	[269]
$[Fe_3(4^iPrtrz)_6(H_2O)_6](BF_4)_6\cdot 2H_2O$	Linear trinuclear, two triple *N*1,*N*2 B	[123]
$[Fe_3(4^iPrtrz)_6(H_2O)_6]I_6$	Linear trinuclear, two triple *N*1,*N*2 bridges	[123]
$[Fe_3(4^iPrtrz)_8(H_2O)_4]I_6\cdot 8H_2O$	Linear trinuclear, two triple *N*1,*N*2 bridges, two monodentate triazoles	[123]
$[Fe_2(4Phtrz)_5(NCS)_4]\cdot 2.7H_2O$	Dinuclear, triple *N*1,*N*2 bridge	[123]
$Fe_5(4\text{-}p\text{-}Toltrz)_{12}(NCS)_{10}(H_2O)_2$	Supramolecular arrangement of one mononuclear and two dinuclear complexes	[123,127]
$[Fe(bte)_2(H_2O)_2](tosylate)_2\cdot H_2O$	Chain with double bte bridges, two water ligands *trans*	[123]
$Fe(bte)_2(NCS)_2\cdot Fe(bte)(NCS)_2(H_2O)_2$	Supramolecular arrangement of two polynuclear chains, one with double bte bridges and two thiocyanates *trans*, and one with single bte bridges and two NCS and two H_2O *all trans*, chains of the second type run *through* the bridges of the first	[123]
$Fe(bte)_3(BF_4)_2$	Supramolecular arrangement of two interpenetrating cubic polynuclear networks	[123]
$[Mn(btp)_2(NCS)_2]$	Chain with double btp bridges, two NCS *trans*	[123]
$Fe(btb)_2(NCS)_2$	Supramolecular arrangement of double-bridged linear chains interpenetrating a stack of a quadratic networks, NCS *trans*	[123]
$[Fe(btb)_2(H_2O)_2](CLO_4)_2$	Stack of two alternating quadratic layers, H_2O *tran*s	[123]
$Fe(btx)_2(NCS)_2$	Stacking of 2d layers, iron atoms in each layer connected by single btx bridges, thiocyanates *trans*	[123]
$[Ag_2(tp)_2](NO_3)_2$	Dinuclear, double *N*3,*N*4 bridge	[270]
$[Ag_2(tp)_2]SO_4\cdot 2H_2O$	Dinuclear, double *N*3,*N*4 bridge	[270]
$[Ag_2(tp)_3]SO_4\cdot 4H_2O$	Dinuclear, triple *N*3,*N*4 bridge	[270]
$[Ru(dmtp)_2(H_2O)Cl_3]\cdot H_2O$	Mononuclear, *N*3 dmtps *trans*	[196]
$[Ru(admtp)_2(H_2O)Cl_3]\cdot H_2O$	Mononuclear, *N*3 admtps *trans*	[271]

Several important properties of the triazoles are the cause of this widespread interest. Because of the position of the donor atoms in the five-membered ring, the triazoles appear to possess the possibility of linking (transition) metal ions together. The triazole ligands thereby constitute a bridge between the metal ions. This bridge can be of several different geometries, depending on the donor atoms of the ligand and the properties of the metal.

Among coordination chemists there is a rapidly growing interest in dinuclear, oligonuclear and polynuclear metal complexes. This arises from the awareness that pairs or clusters of metal ions appear to mediate certain chemical reactions differently from complexes of isolated metal centres. In nature, many metalloproteins appear to have active sites comprising pairs of metal ions in close proximity. Much research is also devoted to mimicking these enzymatic reactions by functionalized models or using such complexes in reactions other than the enzymatic ones. The fact that 1,2,4-triazoles are quite similar in geometry to imidazoles, which occur overwhelmingly in nature, is a second property that has made the triazoles and triazole complexes much sought after compounds to mimic natural processes. They are also used to mimic imidazoles in model compounds for such processes [18]. Also, the substitution of pyrazole ligands by triazoles is being investigated and offers many exciting possibilities, for instance in the research of tripyrazolylborates [19]. The 1,2,4-triazoles are being widely used as pharmaceuticals and as agricultural chemicals and this may be connected to this similarity in geometry as well as coordinative properties.

Another property of triazoles as ligands is that the ligand strength is just in the region to give spin crossover compounds with iron(II) salts. Depending on the substituents the transition temperatures range from about 100 to 400 K. This property means that triazole complexes of iron(II) are studied in the search for spin crossovers at room temperature (r.t.). Such systems are applicable for information storage [20,21]. A review on iron(II) triazole complexes was published in 1996 [22].

Mononuclear metal-triazole complexes are rare especially for first-row transition metals. Provided there are no steric restraints, didentate (bridging) coordination of the triazole ring is the rule. For triazolate ions tridentate coordination is frequently found [23]. Even if the triazole ring is bound to only one metal, the additional nitrogen lone pair may be involved in hydrogen bonding. Compared with pyrazoles and imidazoles, the bonding of the 1,2,4-triazole ring in metal complexes has one link more. Of course these arguments also hold for 1,2,3-triazole rings and there are many similarities between 1,2,4-triazole complexes and those of the almost exclusively studied 1,2,3-triazole: benzo-*v*-triazole. Yet here the steric demands of the vicinal arrangement of the nitrogens has a stronger influence on the bonds in which they participate.

A comprehensive review of metal complexes with 1,2,3-triazoles, tetrazoles and other cyclic catenated nitrogen ligands has been published in *Advances in Inorganic Chemistry*, vol. 32 [24]. An interesting discussion on steric effects involved in the coordination of heterocyclic nitrogen donor ligands is given in *Comprehensive Coordination Chemistry* [18].

Comparing 1,2,4-triazoles with tetrazoles, one would expect for the latter ligands an even greater tendency to oligonucleation. Initially the contrary seemed to be true however. Most of the earlier well-defined tetrazole complexes are mononuclear with monodentate tetrazole ligands. The reason for this is not clear. Steric reasons as with the 1,2,3-triazoles may play a role. Many oligonuclear complexes exist with the *unsubstituted* tetrazolate ion. Because of their comparable σ-donor properties to metals, further research on the 1,2,3-triazoles and tetrazoles as ligands is highly desirable.

Reviews on the coordination chemistry of triazoles have appeared only as sections of papers of a wider scope: organic chemistry of triazoles [6], nitrogen-donor ligands [18], and magnetochemistry [22,25].

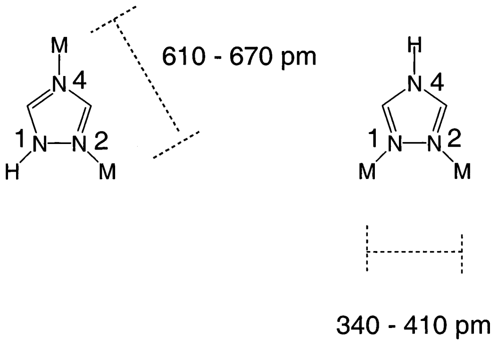
In this paper attention will be focused on the diversity of the geometries of the 1,2,4-triazole complexes and in particular on the structure of oligonuclear metal compounds in which the triazoles constitute the linking ligands. Investigation of the crystal structures of the triazole complexes, however, have shown that the geometry of triazole complexes is rarely simple and in many cases rather different from what one might expect on the basis of the chemical composition.

2. Bridging modes of 1,2,4-triazoles

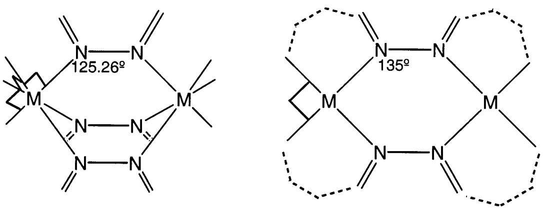
2.1. Bridging mode N1,N2

The bridging mode *N*1,*N*2 is the coordination mode usually found for many triazoles of which the *N*4-position is substituted (see Scheme 1). In this *N*1,*N*2 mode the two metal ions are brought close together at distances of about 400 pm by the first bridging ligand. Because of this, a second and a third ligand, preferably negatively charged, are needed to ‘ease’ the effect of the repulsion of the two metal ions [26,27] (see Scheme 2).

For triazoles with bulky substituents on the 3 or 5 positions, the third ligand may be replaced by a small bridging anion like F^- [28,29] or NCS^- [30]. When bridging anions themselves are bulky there may only be room for one triazole bridge, in

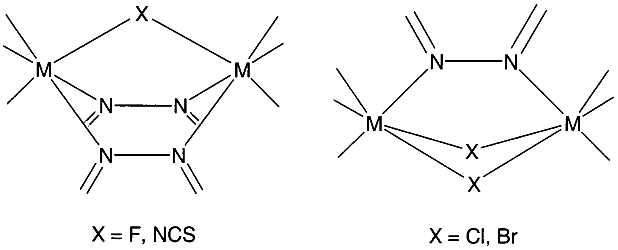


Scheme 1. Geometry of bridging modes of 1,2,4-triazole.



Scheme 2. Triple and double *N*1,*N*2 bridging modes.

addition to two bridging anions, as in the polynuclear compounds [Cu(Htrz)Cl_2] [2] and [Cu(Htrz)Br_2] [31] (see Scheme 3).



Scheme 3. *N*1,*N*2 bridging in combination with single atom bridges.

For the often encountered triple triazole *N*1,*N*2 bridge the metal ions are on a trigonal axis and the coordination angles N–M–N around the metal ions are all 90°, the M–N–N angles are ideally 125.26°. This angle is so close to the angle of the exocyclic free donor electron pair of a regular five-membered ring, 126°, that this triple bridge can be formed without appreciable strain. Many complexes of triazoles show the triple *N*1,*N*2 bridge. It is the preferred geometry for coordination compounds of 4-substitued triazoles (see Scheme 2).

Triazoles with chelating substituents at the 3 and 5 positions may form planar double bridges [32]. For such double bridges however, where the two triazoles and the metal atoms are in one plane, the orthogonal coordination angles impose this M–N–N angle ideally to be 135°. The angle is quite different from the lone-pair angle. The effect is that some strain is produced in the bonds of the bridge: the N–M–N angles distort to about 92° and the M–N–N angles to 132°. This strain is apparently compensated for by the chelate effects (Scheme 2).

2.2. Bridging mode N2,N4, two-dimensional structures

The *N*2,*N*4 bridging mode of the triazoles leads to metal ions at a distance of ca. 650 pm. Complexes of composition [M$(Htrz)_2(NCS)_2$] and M = Cr, Mn, Fe, Co, Ni, Cu, Zn [33] are two-dimensional, layered, compounds.

With 3,5-diaminotriazole (guanazole) and manganese or cadmium thiocyanate a similar bridging mode was found [34,35]. Substitution of *N*1 and *C*5 by condensation of an aromatic six-membered ring also led to layered structures with the *N*2,*N*4 bridge [36].

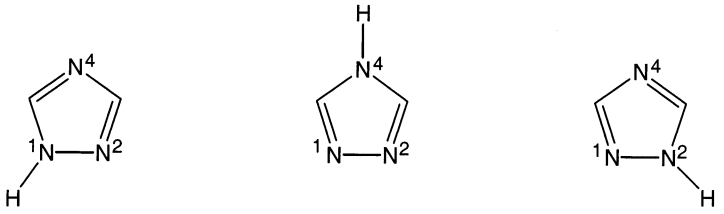
Finally, this 'long' bridge occurs in dinuclear ruthenium and osmium complexes of triazoles with chelating substituents. Examples are compounds of general formula $[M(bpy)_2(3,5\text{-}R_2trz)M'(bpy)_2]^{3+}$ in which M and M′ are Ru, Os, Rh and/or Ir and R is pyridyl[2], pyrazin-2-yl and bpy replaced by 2-phenylpyridine for Rh or Ir [37,38].

2.3. Bridging mode N1,N2,N4, anionic triazole

Anionic 1,2,4-triazole is encountered in planar systems where it bridges between three metal ions. The bridging is a combination of the two double bridges of Scheme 1. A triazolatozinc chloride complex was solved by Krüber in 1995 [39]. The tridentate triazolate bridge is also described for many combinations of Rh, Ir, Pd, and Au by the Oro group [23,40–42]. The triazolates are further discussed in the next section on unsubstituted triazole.

3. Unsubstituted 1,2,4-triazole

Several complexes with unsubstituted triazole and its anion were studied for their magnetic properties as early as 1965 [43,44]. The results were interpreted on the basis of the complexes being polynuclear, however, several structures have never been solved. Although 1,2,4-triazole is a simple molecule and a non-expensive chemical, only 18 X-ray structures of complexes with the unsubstituted triazole are known today. Most likely this is caused by the fact that this ligand almost always immediately produces a microcrystalline, insoluble precipitate with transition metal ions [45–49]. In addition to the ligand–metal interactions, hydrogen bonding plays a most important role in the geometry of the coordination compounds of these ligands. When a triazole ring is involved in a hydrogen bond it is either because the ring still carries an active hydrogen atom bound to one of the nitrogen atoms, or because the ring acts as a hydrogen acceptor *via* one of its nitrogen lone pairs. Of course both options are also possible simultaneously. This is very clearly demon-



Scheme 4. Tautomers of 1,2,4-triazole.

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[2] Throughout this paper for reasons of simplicity the word *pyridyl* is used instead of *pyridin-2-yl*.

strated by the structure of the unsubstituted free ligand. 1,2,4-Triazole itself has three NH-tautomeric forms as shown in Scheme 4.

In the solid state 1,2,4-triazole molecules are asymmetrically arranged [50–52]. The structure has a chain-like hydrogen bonding system in which the hydrazinic *N*1 is donor and *N*4 is acceptor. Clearly the tautomer in the solid is exclusively the 1*H*-tautomer. However, stabilisation of the 4*H*-tautomer is possible in coordination compounds in which both hydrazinic nitrogens are bound to a metal ion. Measurements [53] of the dipole moment of solutions in dioxane of 1,2,4-triazole have indicated that some amount of the 4*H*-tautomer is present. Using ^{14}N-Nmr spectroscopy 40% of the 4*H*-tautomer was calculated to be present in concentrated solutions in methanol [54].

The dependence on pH of the formation of α-Ni(Htrz)$_2$(NCS)$_2$ (pH $\sim$ 7) and β-Ni(Htrz)$_2$(NCS)$_2$ (pH $<$ 4), in which the triazole tautomers are 4*H* and 1*H*, respectively [55], is in accordance with an easily influenced equilibrium for this tautomerism. Infrared spectroscopy was shown to be an excellent tool to discriminate between the two tautomers. The existence of these two isomers illustrates two bonding modes of the 1,2,4-triazole ligand: *N*1*N*2-bridging and *N*1*N*4-bridging. As discussed in the preceding section, the *N*1*N*4 bridging is relatively rare compared with the *N*1*N*2 bridging, which is very common in complexes of first-row transition metals.

The *N*2,*N*4 bridging mode of the triazoles leads to two-dimensional, layered, compounds. A series of composition [M(Htrz)$_2$(NCS)$_2$] was prepared [56] with unsubstituted triazole and M = Mn, Fe, Co, Ni, Cu, Zn. These compounds are two-dimensional networks of metal ions, each connected to four neighbours by bridging triazoles. The *N*-bonded thiocyanates coordinate *trans* to the metal. The SCN–M–NCS axis makes an angle of 30° with the normal to the layers (see Fig. 1). The exchange between the paramagnetic metal centres is antiferromagnetic, except for copper where a small ferromagnetic exchange was measured [33]. The layers can be considered as quadratic magnetic 2-d lattices for which the general theoretical predictions apply for susceptibility and heat capacity [33,57–65]. The two-dimensional Ising behaviour of [Fe(Htrz)$_2$(NCS)$_2$] was further studied by magnetic dilution studies [66].

With 3,5-diaminotriazole (guanazole) and manganese thiocyanate a complex with a similar layer structure could be prepared [27]. The fact that this occurs with the diamino substituted ligand but not with 3,5-dimethyltriazole is another illustration of the importance of hydrogen bonds interactions in triazole chemistry.

Substitution of *N*1 with methyl or phenyl did not give similar two-dimensional compounds, probably due to steric hindrance and lack of stabilization by hydrogen bonding. However, substitution of *N*1 and *C*5 by condensation to an aromatic six-membered ring leads to a triazolopyrimidine, which again gave similar layered structures with thiocyanates through the *N*2,*N*4 bridging [36].

The first structure of a triazole complex proven by single-crystal X-ray determination [2] is the chain structure of Cu(Htrz)Cl$_2$, prepared by dissolving copper(II) triazolate in hot, strong hydrochloric acid, the copper atoms are connected through bridges consisting of a *N*1*N*2-triazole bridge and two asymmetric bridging chlorides

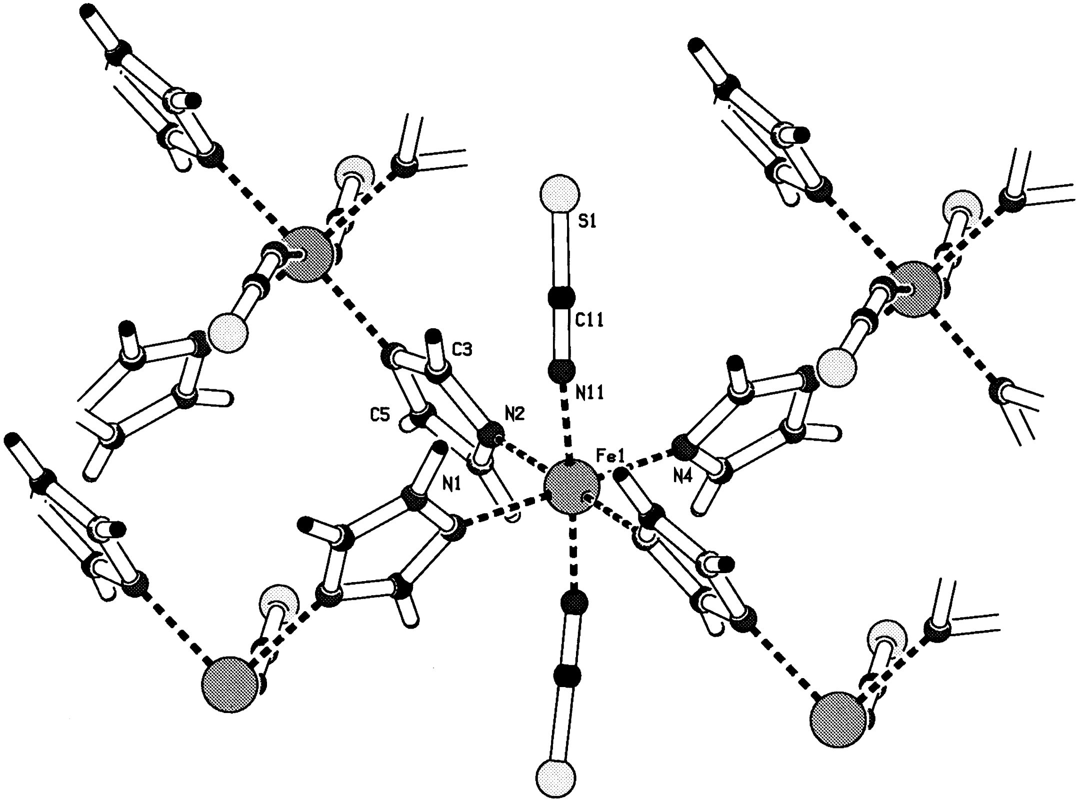

Fig. 1. Schematic representation of the two-dimensional structure of $Fe(Htrz)_2(NCS)_2$ [65].

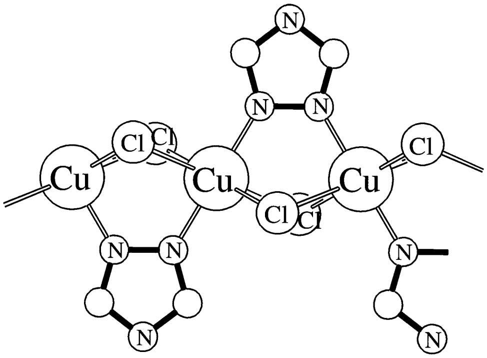

Fig. 2. Schematic representation of the one-dimensional structure of Cu(Htrz)Cl_2 [2].

(see Fig. 2). The compound is extensively studied by infrared spectroscopy [67,68], EPR and optical-absorption studies [69] and magnetic measurements [25,43,44,70–75]. The analogously prepared bromide Cu(Htrz)Br_2 has the same structure [31].

The second complex of a triazole which the structure was determined by X-ray diffraction, $[Ni_3(Htrz)_6(H_2O)_6](NO_3)_6$ [3,4], was prepared from nickel nitrate and triazole in water. It has a linear trinuclear cation, a structure which is nowadays known to be very common for 4-substituted triazoles (see Fig. 3). Its magnetic properties have been studied and calculated for a linear system of three $S = 1$ ions [76,77].

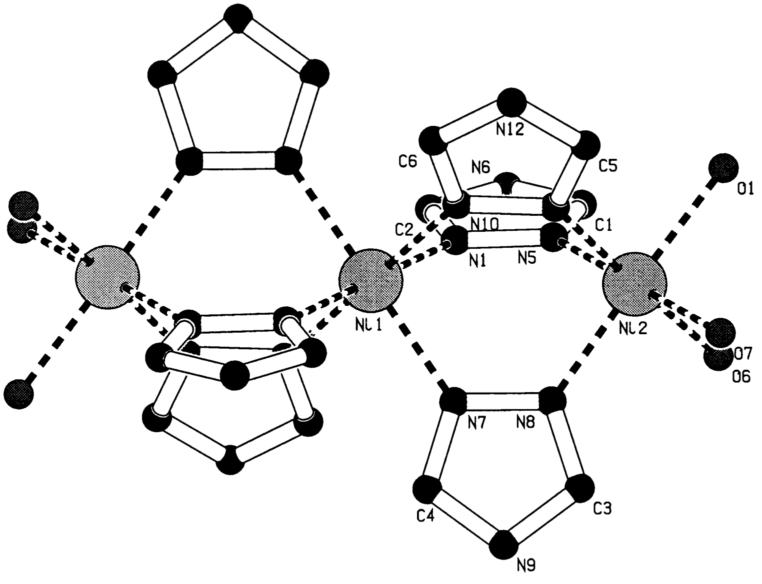

Fig. 3. Structure of the cation of $[Ni_3(Htrz)_6(H_2O)_6](NO_3)_6$ [3].

Azole complexes with silver were already reported in 1893 [78,79], and the interest in this class of compounds has continued ever since, owing to their (potential) application in photography and silver plating [80,81]. The first structure of a silver complex with unsubstituted triazole was reported in 1991. It was synthesized from triazole and silver nitrate in aqueous ethanol acidified with nitric acid. The complex appeared to be dinuclear with a double *N*1,*N*2 bridge. The hydrogen on N4 is involved in a hydrogen bond to a nitrate ion [82].

A factor of importance in the synthesis of compounds with 1,2,4-triazole is the ease of formation of the triazolate ion by deprotonation. An example is the compound [Fe(Htrz)$_2$(trz)]BF$_4$ [45]. This complex is a polynuclear chain in which the iron atoms are connected by a triple triazole bridge of which one triazole is deprotonated. The structure was elucidated by EXAFS [83] and XAS [84] measurements. This compound and a related one of composition [Fe(Htrz)$_3$](BF$_4$)$_2$ with an analogous structure and similar ones with other anions were studied for their spin crossover properties [14,49,85–87]. Most of them are purple to pink complexes of the low spin type at r.t. On heating to about 100°C they change to white high spin compounds. Upon cooling, the process is reversed often with an appreciable hysteresis effect. This is shown in Fig. 4 for the compound [Fe(Htrz)$_2$(trz)]BF$_4$, which was prepared for the first time in 1977. This compound has been studied extensively because of its potential application in data storage materials [88]. The structure consists of a polynuclear chain with triple bridges. This was also derived from the fact that virtually all iron ions change their spin state so that the chromophore must be FeN$_6$. Stability in the chain is further gained by the charge of 1 − of each three ligands. The triple mixed ligand triazole/triazolate bridge can be compared with a similar triple bridge of charge 2 − in a trinuclear cobalt(III) complex with 3,5-diaminotriazole, described in Section 4. The compound [Fe(Htrz)$_2$(trz)]BF$_4$ is X-ray isomorphous to analogous Mn, Co and Zn compounds [45]. The BF$_4$ anion can be substituted by ClO$_4$ and PF$_6$ [86].

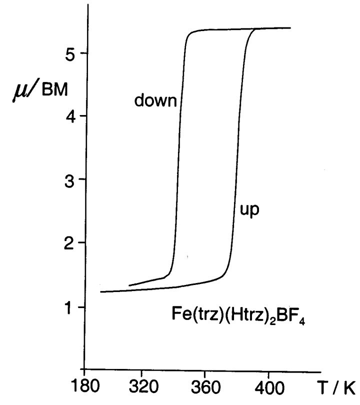

Fig. 4. Magnetic moment vs. temperature of [Fe(trz)(Htrz)$_2$]BF$_4$ [22].

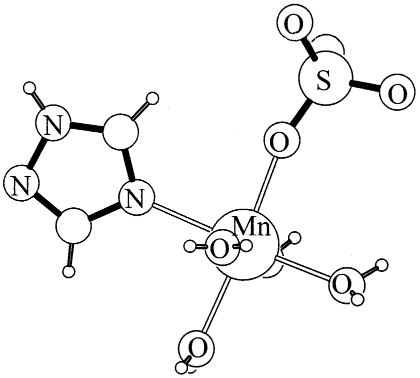

Fig. 5. Monodentate coordination of 1,2,4-triazole in [Mn(Htrz)(H_2O)$_4$$SO_4$] [95].

Triazolates of copper and silver have been known for many years [1,89]. Copper(II) salts were studied for their magnetic properties [25,43,44,70,73]. Triazolates of zinc, cadmium, nickel and cobalt were first studied in 1974 [90], further in 1978 [46,91], but X-ray structures appeared much later. Zn(trz)Cl for instance [39], prepared from triazole and zinc chloride in ethanol, is a two-dimensional layered complex in which the triazolates are tridentate, linking the zinc ions into puckered sheets. Each zinc is coordinated to three different triazolate ions and one chloride.

The structures of several second-row transition metal triazolate complexes were determined by Oro [23,40–42,92]. These are mainly complexes of rhodium and palladium in which the triazolate is also bonded between three metal centers. A single *N*1,*N*2 triazolate bridge, combined with two bridging diphenylphosphinomethane ligands was described [93] for [Rh_2(trz)(dppm)$_2$(CO)$_2$]; several similar complexes having the same basic structure were also prepared.

A single *N*1,*N*4 bridge of the unsubstituted triazolate anion was found as the central bridge between the palladium atoms in a tetranuclear (PtPd)$_2$ complex [94].

In few cases is the unsubstituted triazole only monodentate. In all such compounds it coordinates through *N*4. In Mn(Htrz)(H_2O)$_4$$SO_4$ the coordination number of manganese is six, the *N*4 of 1,2,4-triazole is *trans* to a sulfate oxygen. The hydrazinic group is involved in a hydrogen bond network with sulfate and water of neighbouring molecules [95] (see Fig. 5).

Triazole in [Cd(Htrz)$_2$(NCS)$_2$] is also monodentate with donor atom *N*4 and the hydrazinic function is involved in strong hydrogen bonding of the closed dimer type [96] (see Fig. 6).

The imino nitrogen atom thus seems to be the preferred donor for coordination even when the hydrazinic group is not involved in strong hydrogen bonding. This is shown by the structure of [Fe(bpy)(Htrz)Cl_3] in which only weak hydrogen donor bonding to chloride is present, yet again triazole coordinates through *N*4 [97].

In the determination of the crystal structure of 1,2,4-triazole to the zinc in human carbonic anhydrase II, the triazole also coordinates through N4 to the metal [98]. This was concluded from the nature of the groups interacting with the triazole ring in the peripheral position through hydrogen bonding.

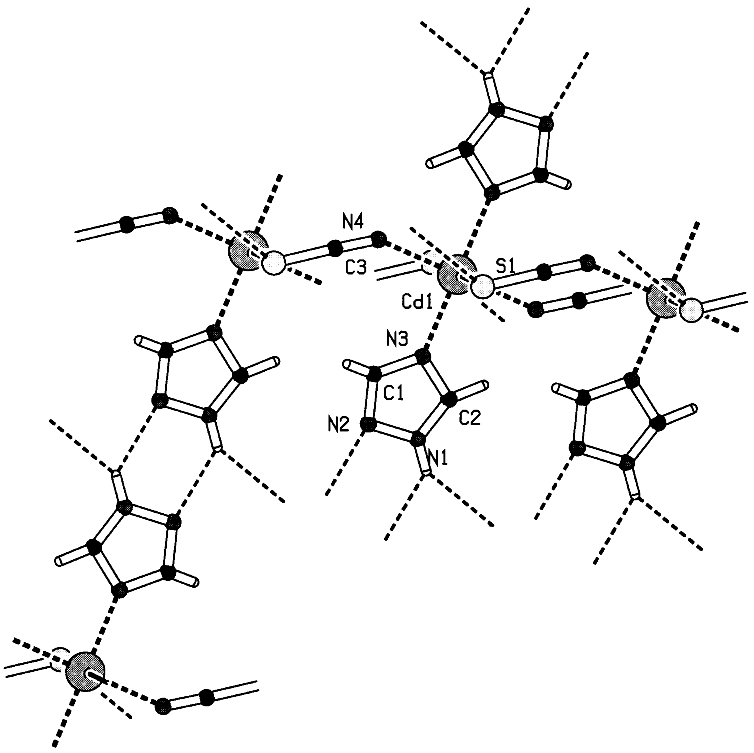

Fig. 6. Structure of $[Cd(Htrz)_2(NCS)_2]$ showing the hydrogen bridge system [96].

Electronic spectra in the UV–vis regime were used to show [99] that the triazole ligand coordinates via *N*4 to the metal centers in the complex ions $[Fe(CN)_5(Htrz)]^{2-}$ and $[Ru(NH_3)_5(Htrz)]^{3+}$.

4. Complexes with 4-substituted triazoles

By blocking the *N*4 donor position through substitution, only the *N*1 monodentate and the *N*1*N*2-didentate coordination modes are possible. Both have been observed and, moreover, sometimes in the same coordination compound.

Triazole ligands substituted on *N*4 are 4-amino-1,2,4-triazole, 4-alkyl- and 4-aryl-1,2,4-triazole. A special case is 4,4′-bi-1,2,4-triazole.

4.1. 4-Aminotriazole and derivatives

4-Aminotriazole (4atrz) was used as a ligand for the first time by the Larionov group in Novosibirsk [100]. Complexes with composition $M(4atrz)_3(NO_3)_2 \cdot xH_2O$, M = Co, Ni, Cu, Zn, Cd, $x = 0.5$, 1 or 1.5 were prepared. Many papers with this ligand have since appeared [85,101,102]. Iron(II) compounds with this ligand showed spin transitions above r.t. In fact, up until now, the iron(II) complexes of 4-aminotriazole show the highest T_cs found for ion(II). Further research by Kahn [20,103,104] revealed that the magnetic transition temperature could be tuned to r.t. by doping the ligand with 1,2,4-triazole or choosing the right anion. The complexes are of composition FeL_3X_2 and proved to be polymeric by EXAFS measurements [83,84]. Complexes of iron(II) iodide and thiocyanate with 4-aminotriazole were described by Lavrenova et al. [21]. This paper established that the range of T_c values for the spin transition of Fe(II) in $Fe(4atrz)_3A_2$ varied from 210 K for $A = ClO_4^-$ up to 342 K for $A = NO_3^-$. Also, specific heat measurements on $Fe(4atrz)_3(NO_3)_2$ and $Cu(4atrz)_3(NO_3)_2$ have been described [14,105].

The X-ray structure of $Cu(4atrz)Cl_2$ showed it to be a 1-d polymer chain, similar to that of $Cu(Htrz)Cl_2$ [106].

The amino group itself can also be substituted. 4-dimethylamino-1,2,4-triazole was investigated for its coordinating properties by Krůber. A trinuclear iron(II) complex of composition $[Fe_3(Me_2Ntrz)_6(H_2O)_6](ClO_4)\cdot 2H_2O$ with spin crossover properties was found [107] (see Fig. 7).

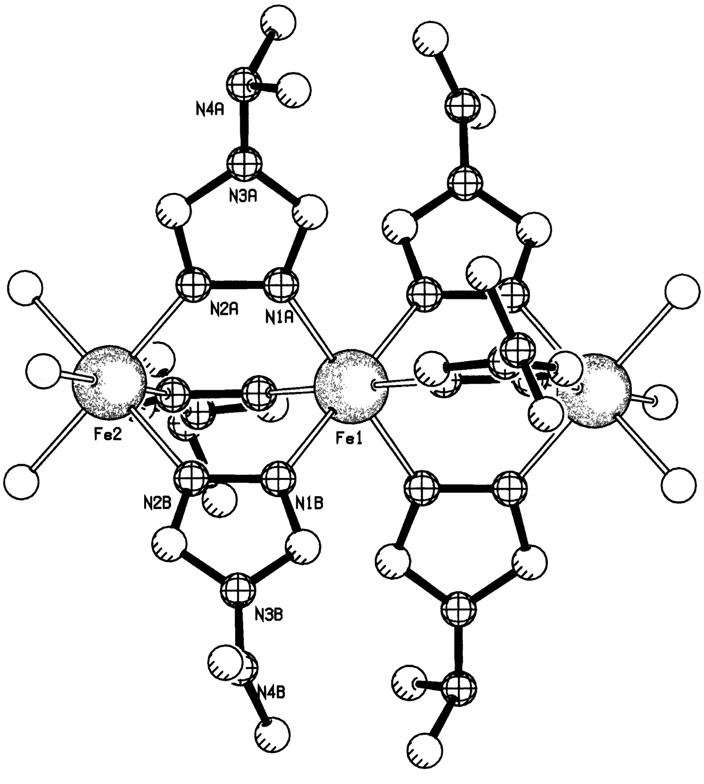

Fig. 7. Schematic representation of the trinuclear cation of $[Fe(Me_2Ntrz)_6(H_2O)_6](ClO_4)_6$ [107].

The 4-amino group can easily be transformed into another 1,2,4-triazole ring. This provides the ligand 4,4′-bi-1,2,4-triazole (btr). The compound was synthesized for the first time by Bartlett and Humphrey [108] and its structure solved by Domiano [109]. The two triazole rings are almost perpendicular to each other. With transition metal thiocyanates two-dimensional polynuclear compounds were found of composition $[M(NCS)_2(btr)_2]\cdot H_2O$ (M = Fe, Co, Ni) [110] (see Fig. 8). The btr ligand forms *N*1,*N*1′ bridges in 2-d layers [111]. The iron compound appears to possess a spin transition with a large hysteresis at 120 K (down) and 140 K (up) [112,113]. The iron selenocyanate complex with the same structure was also studied, it shows T_c down 211 K and up 217 K [114].

Dilution effects on the spin crossover in the iron complex have been studied [17,115,116]. The spin crossover was also studied by VT infrared spectroscopy [117] (see Fig. 9).

Manganese thiocyanate does not give the same structure with this ligand. Complexes of composition $[Mn(NCS)_2(btr)_2]$ [113], $[Mn(NCS)_2(btr)(H_2O)_2]$ [118] and $[Mn(NCS)_2(btr)_3(H_2O)]$ [117] have been described. The latter two are 1-d chain compounds with single *N*1,*N*1′ ligand bridges.

In $[Mn(NCS)_2(btr)_3(H_2O)]$ two of the btr ligands coordinate in the monodentate mode. No tridentate or tetradentate coordination has been found for this ligand up until now. The complex $[Mn(btr)_2(H_2O)_2](NO_3)_2$ [119], however, does form a 2-d layered structure analogous to the structure of $[Fe(btr)_2(NCS)_2]\cdot H_2O$.

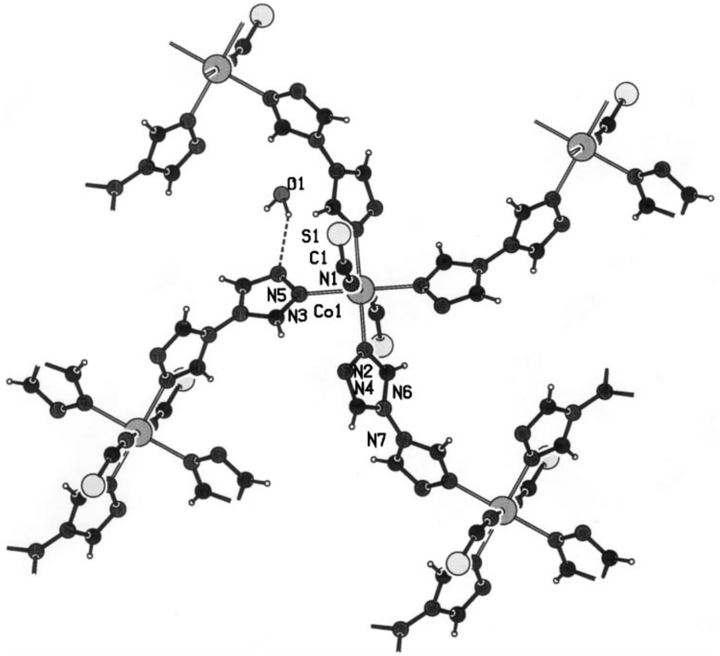

Fig. 8. Structural representation of $[Co(btr)_2(NCS)_2]\cdot H_2O$ showing hydrogen bond [111].

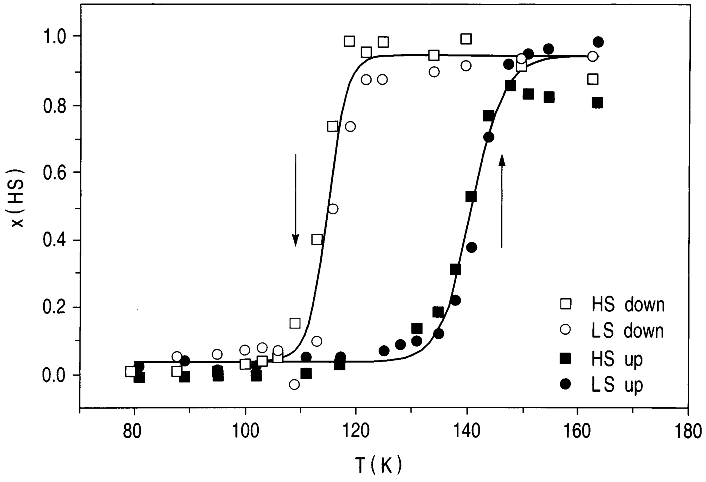

Fig. 9. Hysteresis in spin crossover of $[Fe(btr)_2(NCS)_2]\cdot H_2O$, as determined by VT infrared spectroscopy. Solid line drawn as guidance for the eye [117].

Structures in which the connecting btr bridges constitute a three-dimensional network are rare. An example is the 3-d polynuclear cationic part of $[Co(btr)_3](CF_3SO_3)_2$ [120], of which the large *N*1,*N*1′ bridge of the 4,4′-bitriazole provides for large holes in which the trifluorosulfonate anions are stored (see Fig. 10).

4.2. 4-Alkyl- and aryl-triazoles and derivatives

Triazoles with an alkyl or aryl substituent on the 4-position behave in much the same fashion in the formation of complexes . Dinuclear, trinuclear and polynuclear chains with triple triazole bridges are the preferred structures.

Tetranuclear complexes of the linear type, with three triple *N*1,*N*2-bridges, homologues of the dinuclear and trinuclear compounds do not exist. Many trials to synthesize such compounds have failed and led only to either trinuclear or polymeric compounds.

A few mononuclear compounds are known in which the 4-substituted triazole coordinates through *N*1. An example is $[Cr(CO)_5(4Metrz)]$ [121,122].

With coordinating anions like thiocyanate, chain formation terminates is already terminated with two metal atoms. The composition is then $M_2L_5(NCS)_4$, three triazoles in the bridge, two other triazoles are monodentate. The molecule is symmetric. Examples include $[Mn(4Metrz)_5(NCS)_4]$ [59], $Co_2(4Phtrz)_5(NCS)_4\cdot 5H_2O$ [61] and the isostructural iron compound $Fe_2(4Phtrz)_5(NCS)_4\cdot 5H_2O$, which has a spin crossover at $T_c = 50$ K [123] (see Fig. 11).

The dinuclear complexes can also be asymmetric, for instance $[Ni_2(4Ettrz)_4(H_2O)(NCS)_4]\cdot 2H_2O$ [124–126] in which three triazoles form a bridge and a fourth one is monodentate on one nickel.

A substance of composition $Fe_5(4\text{-}p\text{-Toltrz})_{12}(NCS)_{10}(H_2O)_2$ [123,127] is a pentanuclear supramolecular arrangement of two dinuclear species connected through strong hydrogen bonds to a mononuclear complex. The four iron atoms in the two dinuclear species show the spin crossover effect (see Fig. 12).

Combination of the complexed cations with non-coordinating anions like $CF_3SO_3^-$ affords trinuclear compounds. The structures are all similar to the Reimann and Zocchi complex depicted in Fig. 3. The trinuclear iron(II) complexes of this type show the spin crossover effect for the central iron [26,128].

The trinuclear complexes $[Fe_3(p\text{-anisyltrz})_6(H_2O)_6](\text{tosylate})_6$ and $[Fe_3(p\text{-anisyltrz})_8(H_2O)_4](BF_4)_6$ differ in the fact that two additional monodentate ligands have replaced two water ligands in the second complex. Only the first complex undergoes spin crossover for the central iron on cooling. The difference in behaviour was attributed to a change in the torsion angle between the triazole ring and the benzene ring [129].

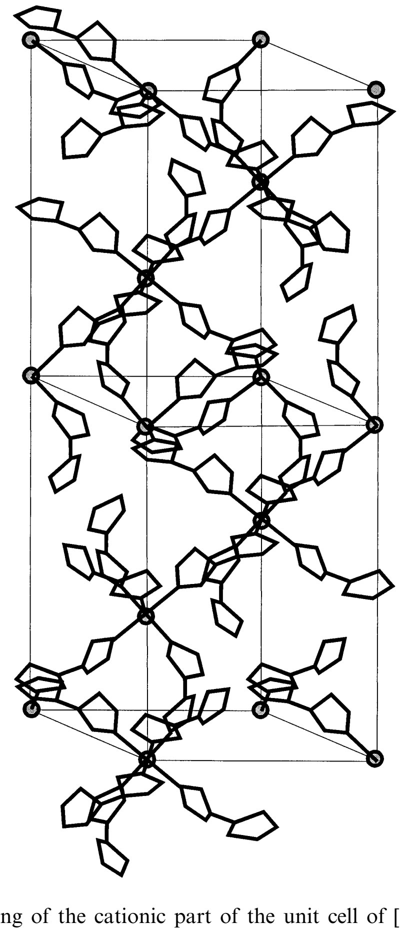

Fig. 10. Schematic drawing of the cationic part of the unit cell of $[Co(btr)_3](CF_3SO_3)_2$ [120].

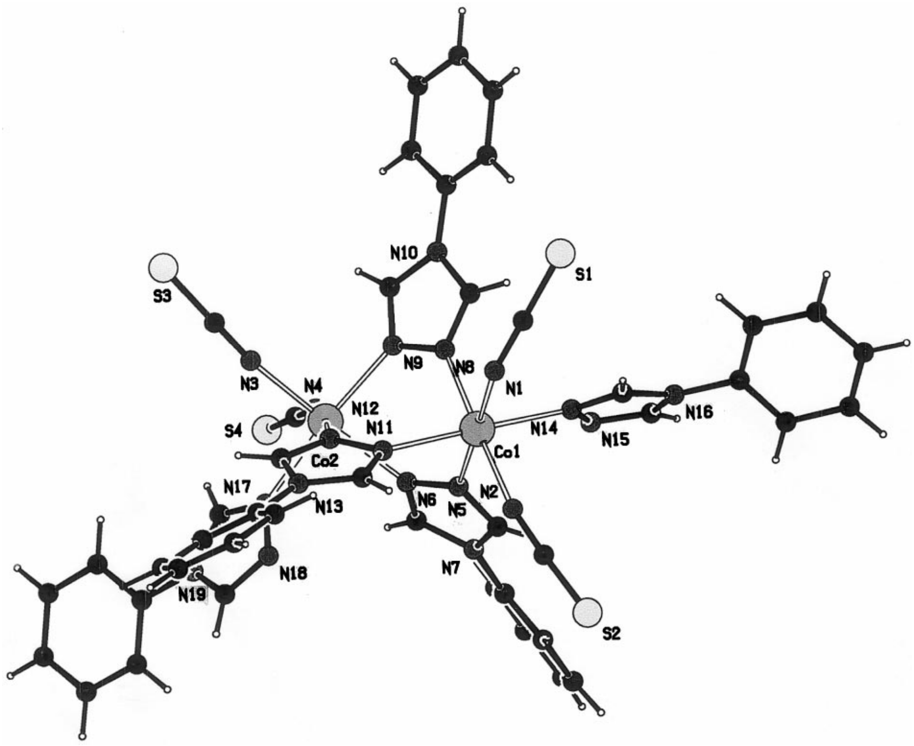

Fig. 11. Drawing of the molecular structure of $[Co_2(4Phtrz)_5(NCS)_4]\cdot 5H_2O$ showing monodentate and didentate 4-phenyltriazole [61].

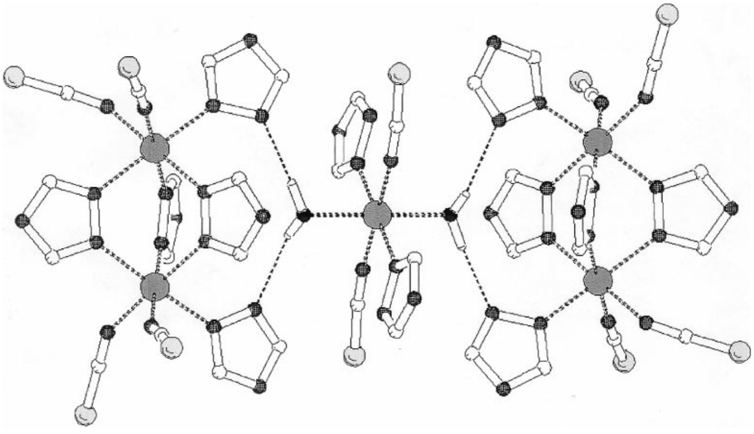

Fig. 12. The pentanuclear assembly $[Fe_2L_5(NCS)_4]_2[FeL_2(NCS)_2(H_2O)_2]$, L = 4-*p*-tolyltriazole; tolyl groups and CH bonds omitted for clarity [123].

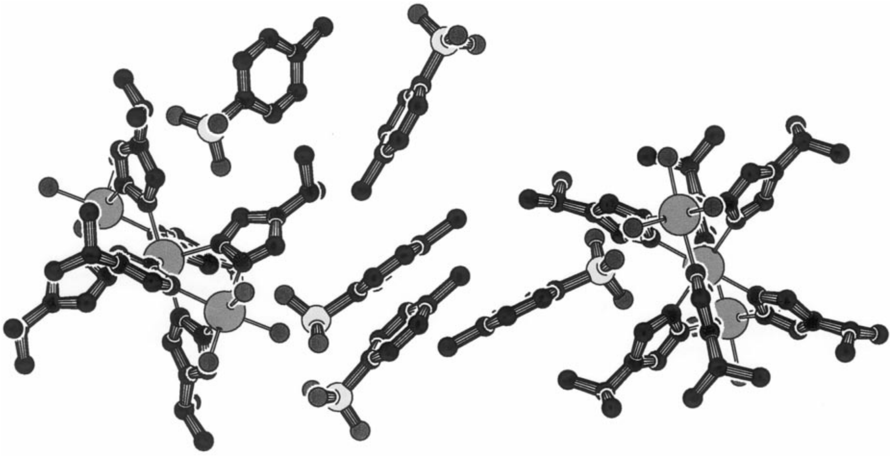

Fig. 13. Schematic drawing of part of packing of $[Fe_3(4^iPrtrz)_6(H_2O)_6](tosylate)_6 \cdot 2H_2O$ showing some stacking of tosylate ions between trinuclear cations, hydrogen atoms omitted [12].

This linear trinuclear structure is very often found for triazoles that have N4 substituted, and sometimes also when non-bulky substituents on the 3 and 5 positions are present (see also Section 4).

Another example is the blue trinuclear $[Fe_3(4^iPrtrz)_6(H_2O)_6](tosylate)_6 \cdot 2H_2O$[12]. It has a very gradual spin crossover between about 200 and 350 K (see Fig. 13).

When the substituent on *N*4 is very bulky there appears to be less tendency to polynucleation, $[Zn(4^tButrz)_2(NCS)_2]$ [130] is mononuclear. With the larger cadmium ion, however, an alternating 1-d chain is formed [131] (see Fig. 14).

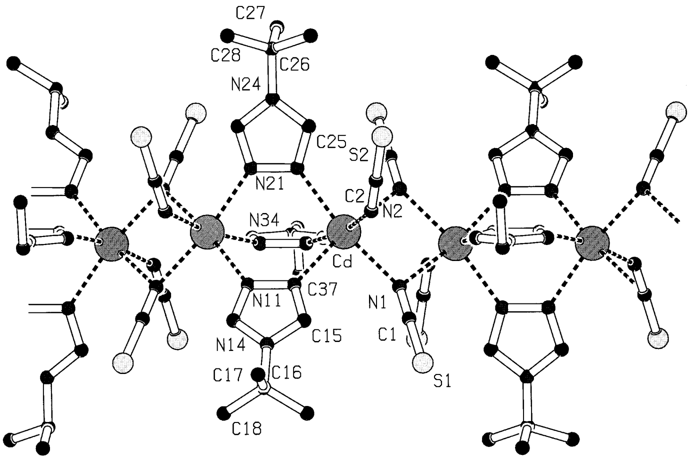

Fig. 14. Part of the chain structure of $[Cd_2(4^tButrz)_3(NCS)_4]_\infty$ showing alternating triazole and thiocyanate bridges [131].

Chains are also supposed to occur in complexes of composition FeL_3A_2 in which L is a 4-alkyl substituted triazole and A a monovalent anion. The dependence of T_c on the spin crossover, on the alkyl chain length and on the size of the anion has been studied by Kolnaar [123]. The smallest anion (chloride) gave the highest T_c and the largest hysteresis. The effect of the alkyl groups was less pronounced, yet methyl and ethyl substituents gave the highest T_cs for both chloride and for tetrafluoroborate: $[Fe(4Metrz)_3](BF_4)_2$ $T_c\downarrow 247$ K, $T_c\uparrow 245$ K, $[Fe(4Ettrz)_3](BF_4)_2$ $T_c\downarrow 231$ K, $T_c\uparrow 249$ K, $[Fe(4Metrz)_3]Cl_2\cdot 3H_2O$ $T_c\downarrow 325$ K, $T_c\uparrow 382$ K, $[Fe(4Ettrz)_3]Cl_2\cdot 3H_2O$ $T_c\downarrow 310$ K, $T_c\uparrow 365$ K.

A 4-substituted triazole with a donor group on the substituent is 4-(2′-hydroxyethyl)-1,2,4-triazole. With copper perchlorate this ligand gives a polynuclear structure in which the parallel chains are stabilized by hydrogen bridges involving the ethyl-hydroxyl groups [132]. With the ligand 1,2-bis(triazole-4′-yl)ethane a compound of composition $Cu_3L_5(ClO_4)_6\cdot 2H_2O$ is prepared. It consists of interconnected trinuclear units with the usual triple *N*1*N*2 bridges [133].

5. Complexes of 3,4,5-alkyl substituted 1,2,4-triazoles

Triazoles with non-chelating substituents in 3, 5 and/or 4-positions coordinate in either *N*1 monodentate or *N*1,*N*2 didentate fashion. In this respect they very much resemble the 4-substituted triazoles [134,135]. Those ligands with chelating groups in 3 and/or 5-position behave differently, and are treated in a separate section (Section 6).

In the well-known triple *N*1,*N*2 bridging mode the steric demands of (bulky) substituents on the 3 or 5 positions it is found that the third ligand may be replaced by a small bridging anion. Ligands like 3,5-dimethyltriazole, 3,4,5-trimethyltriazole and 4-amino-3,5-dimethyltriazole form such trinuclear compounds with metal fluorides [28,29], or thiocyanates [30]. In this last case the rarely encountered *N*-bridging thiocyanate is found (see Fig. 15).

To this class the group of 3-amino-5-alkyl-1,2,4-triazoles ligands prepared from aminoguanidine and carboxylic acids also belong. A complex which the X-ray structure was solved is $Zn((atrz)_2CH_2)_2F_2$ [136] (see Fig. 16).

Several copper trinuclear complexes were described with 1,9-bis(3-aminotriazol-5-yl)-3,7-dithianonane [137]. The bridging between the copper atoms is double *N*1,*N*2-triazole, single chloride. The sulfur atoms are involved in the coordination of the non-central copper atoms. The use of the $ZnCl_4^{2-}$ anion gave a $ZnCu_3Zn$ pentanuclear coordination compound (see Fig. 17).

A cyclic trinuclear copper(II) complex anion of composition $[Cu(35Me_2\text{-}4atrz)Cl_2)_3OH]^-$ was prepared with 3,5-dimethyl-4-aminotriazole. The copper ions are bridged in pairs by *N*1,*N*2 coordinating triazoles and in the centre is a hydroxide. A H_3O^+ cation compensates the negative charge [138].

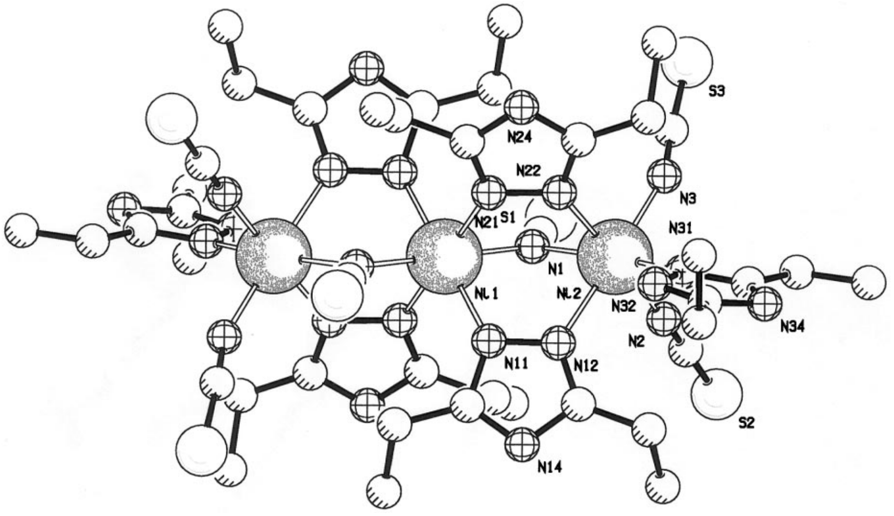

Fig. 15. Schematic representation of the structure of $[Ni_3(35diEttrz)_6(NCS)_6]{\cdot}2H_2O$ [30].

Finally, there is the ligand 3,5-diaminotriazole (guanazole) with which several compounds have been prepared [27,139]. Apparently because the substituents on positions 3 and 5 are capable of forming hydrogen bonds, the linking of metal ions by triple bridges is preferred here. This ligand gives trinuclear complexes with nickel thiocyanate and cobalt chloride. The last compound, $[Co_3(Ha_2trz)_2(a_2trz)_4(H_2O)_6]Cl_3{\cdot}9H_2O$ shown in Fig. 18, is very remarkable because of the mixed valences of the cobalt ions and the triazole/triazolate mixed ligand bridges. The central Co^{3+} ion is comparable to the central Fe^{2+} low spin in the trinuclear iron

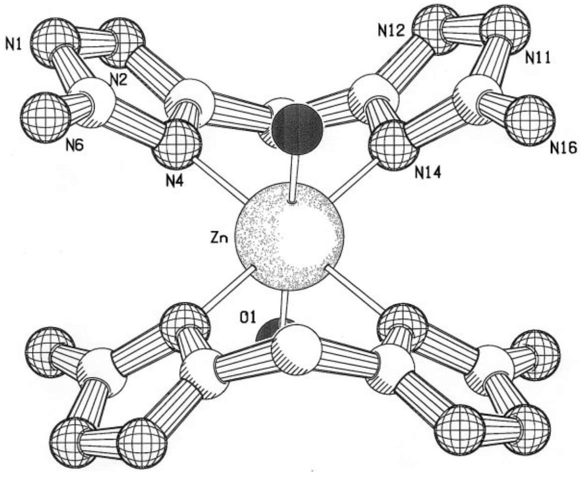

Fig. 16. Structure of the cationic part of $[Zn((3atrzH)_2CH_2)_2(H_2O)_2]F_2$ [136].

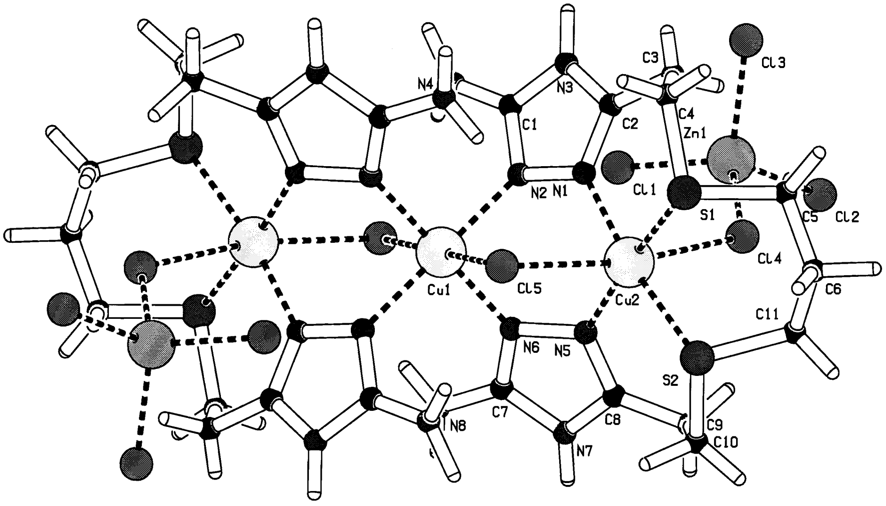

Fig. 17. Structure of the molecular unit of $[Cu_3(attn)_2Cl_2(ZnCl_4)_2]$, attn = 1,9-bis(3-aminotriazol-5-yl)-3,7-dithianonane [137].

compounds described above. Clearly the bringing together of the three cobalt ions of total charge 7+ with a Co^{2+}–Co^{3+} distance of 365 pm needs a negatively charged bridge, in this case each triple bridge is 2−.

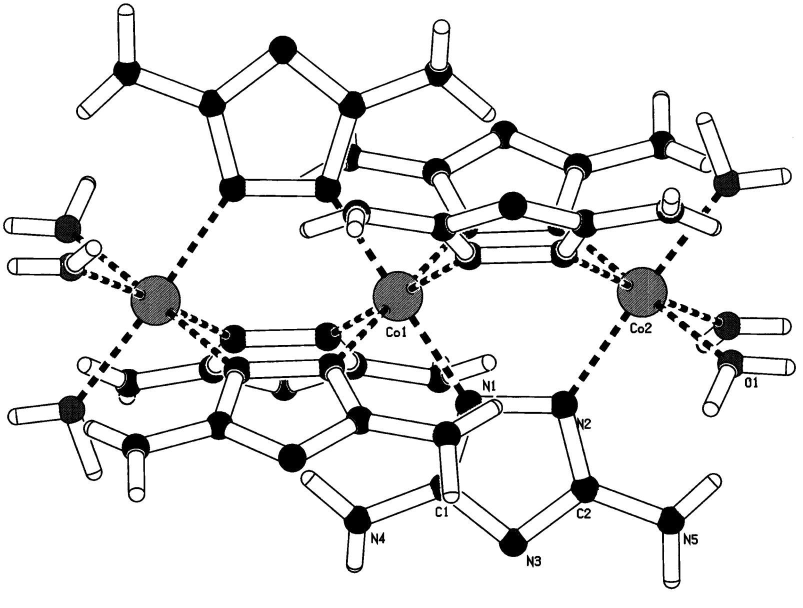

Fig. 18. Cationic part of $[Co_3(Ha_2trz)_2(a_2trz)_4(H_2O)_6]Cl_3{\cdot}9H_2O$ [27].

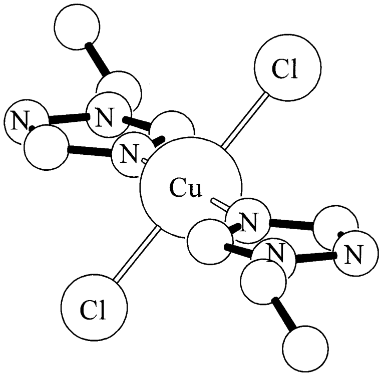

Fig. 19. Molecular structure of [Cu(1Ettrz)$_2$Cl$_2$] [140].

6. 1,2,4-Triazoles substituted on N1

Triazoles with substituents on N1 may be divided in two main groups. The first are the alkyl and aryl substituted triazoles. The second group are the triazolylborates. The donor atom of the first group is *N*4, obviously the other coordination site, *N*2, is sterically disfavoured by the neighbouring substituent. The earliest example is CuCl$_2$(1Ettrz)$_2$ [140], which has copper in a square-planar coordination and the ligands coordinate via *N*4 in *trans* position (see Fig. 19).

Complexes of 1-phenyltriazole were studied by Donker [141]. Compositions ranged from M(1Phtrz)$_4$(NCS)$_2$ (different isomers) to M(1Phtrz)$_2$(NCS)$_2$. The X-ray structures of several mononuclear compounds were investigated by Aret [142].

The synthesis of a 1-pyridyltriazole complex, [Ru(bpy)$_2$(1Pytrz)](PF$_6$)$_2$, was described by Hage [143], this ligand, being a chelating ligand, utilises *N*2 as the donor atom.

Kolnaar [123] studied the complexing behaviour of α,ω-bis(triazol-1-yl)alkanes. These ligands give supramolecular structures with interwoven 1D, 2D and 3D networks. The triazole donor atom is *N*4. The complex Fe(btb)$_2$(NCS)$_2$ in which btb is 1,4-bis(triazole-1′-yl)-butane is a 2D layer system interwoven with 1D chains, schematically depicted in Fig. 20.

A new chapter both in triazole chemistry and in the chemistry of the azolylborates is the discovery of complexes of triazolylborates (and tetrazolylborates) [144], at first combined with molybdenum [145,146] and further developed by the group of Janiak in Berlin [7]. The additional donor sites of the triazolyl groups offered many different coordination modes. Hydrogen bonds [147] between remaining nitrogen donors and water molecules contribute to the stability of the structures [19]. In addition to this, also here, the triazole ligand has the possibility to bring Fe^{2+} in a spin crossover position [148,149]. Compositions of the tristriazolyl borate complexes are M(ttb)$_2$·6H$_2$O (M = Fe, Co, Ni, Cu, Zn), in these complexes the donor atom of the triazole is *N*2 [149]. However, linkage isomerism can occur in which the donor atom is *N*4, e.g. in the complex Zn(ttb)$_2$·1.5H$_2$O [150]. The combination with coordinating anions affords polynuclear structures: $Cu_2Cl_2(ttb)_2\cdot 2H_2O$ is a 2-d double layer; in $[Cu_2(OH)_2(ttb)]Cl\cdot 6H_2O$, a 3-d structure, half of the copper ions are coordinated to three *N*2 donors, the other half to three *N*4, in addition to hydroxide oxygens [151]. With silver a 2-d structure was found [152].

Polynuclear structures comparable to those of the complexes of the bistriazolylalkanes have been described for the ditriazolylborates [147,153].

7. 3,(5)-Substituted triazoles with chelating substituents

As pointed out in Section 2, the deviation of the M–N–N angle from the regular lone pair angle of the five ring in the planar double *N*1,*N*2 bridge is large and additional stabilization for this geometry is necessary. It appears that this geometry preferably occurs if the triazole takes part in at least one chelate ring involved in the coordination around the metal. Examples are abundant for triazoles that have been 3,5-substituted with chelating substituents. Substituents studied are 2-pyridyl, 2-pyrazinyl, acetylamino, aminomethyl, hydroxymethyl and carboxyl (see Table 1).

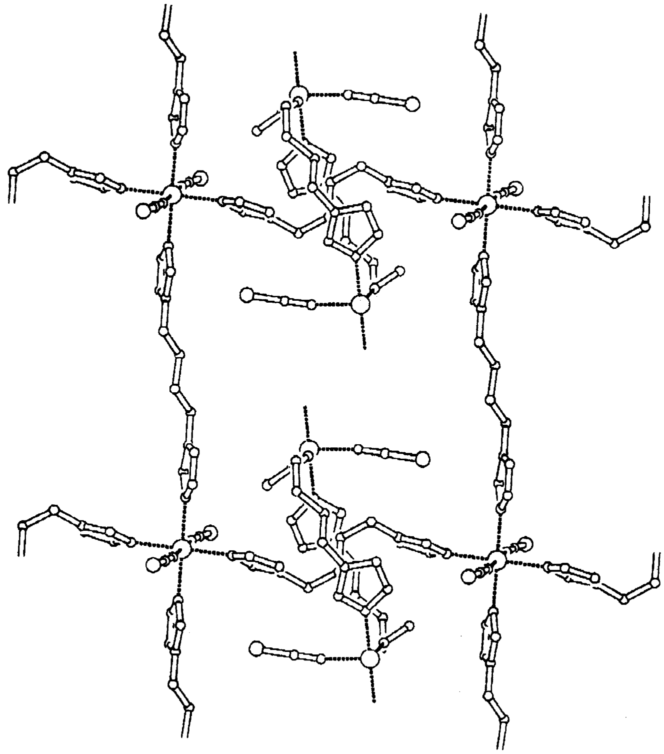

Fig. 20. Representation of the structure of $[Fe(btb)_2(NCS)_2]_\infty$, btb = 1,4-bis(triazol-1-yl)butane. Connecting ligands in one direction of a 2d-grid are embraced by the double bridges of 1d-chains [123].

The combination of the triazole ring with a donating substituent, especially in the 3 and 5 positions, may produce these chelating ligands. The preferred donor atoms are nitrogen and oxygen.

Many reports have been published dealing with the coordination properties of derivatives of triazole-3-thiol. Although such complexes are used as indicators for metal ions, little is known about their structures. Polynuclear structures are very likely because the sulfur atom will not be involved in a chelate ring with the triazole N-donors. Such compounds will not be treated here. However, the sulfur donor, of the thione group tautomer, can form chelates with other substituents of the ring. An example is the compound $[CuLCl_2]\cdot H_2O$ (L = 4-amino-1,4-dihydro-3-methyl-1,2,4-triazole-5-thione). The thione group and the 4-amino group are the donor atoms in a five-membered chelate ring with copper(II) [154].

7.1. N-donors in chelating substituents

Substituents with N donors are most abundant. The pyridyl group is the preferred substituent. With 3,5-dipyridyl-4-aminotriazole Keij [155] synthesized dinuclear transition metal compounds, e.g. $[Ni_2(35Py_2atrz)_2(H_2O)_2Cl_2]Cl_2\cdot 4H_2O$. The bridge is a planar double *N*1,*N*2 bridge (see Fig. 21).

Further research with this ligand not only confirmed its dinucleating nature [156], but showed that it can also be chelating in a mononuclear complex:

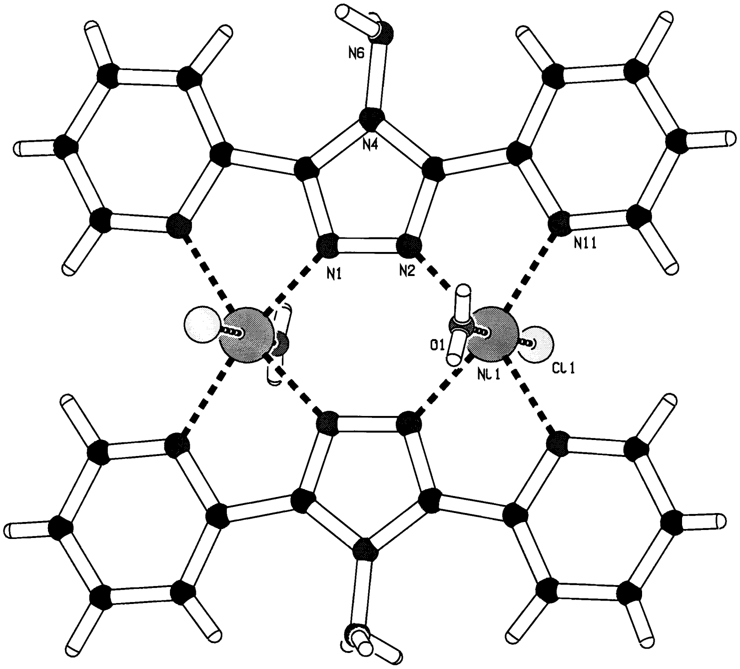

Fig. 21. Skeletal drawing of the structure of the cation of $[Ni_2(35Py_24atrz)_2Cl_2(H_2O)_2]Cl_2\cdot 4H_2O$ [155].

$[Mn(35Py_2atrz)_2(H_2O)_2]Br_2$ [157] and the spin crossover compound $[Fe(35Py_2atrz)_2(TCNQ)_2]$ [158] $T_c = 280$ K.

A remarkable tetranuclear complex of composition $[Cu_4(PyPztrz)_4(H_2O)_4](NO_3)_4 \cdot 12H_2O$ was prepared by Prins from 3-pyridyl-5-pyrazinyltriazole [159] (see Fig. 22).

The coordination properties of the anion of 3,5-dipyridyltriazole towards 2nd and 3rd row transition elements has been the subject of a research programme by Hage [160]. The donating and accepting properties of these and analogous ligands controlling the photophysical and electrochemical properties of ruthenium and osmium mono- and oligonuclear complexes have been investigated in a series of more than 35 papers between 1986 and 1997. A review on the subject has been published [161]. It has been found that for these complexes the properties can easily be tuned by changing the pH of the solution.

For the chelating ligand 3-pyridyltriazole, two linkage coordination isomers ($N2,N'$ and $N4,N'$) of $[Ru(bpy)_2(3PyHtrz)](PF_6)_2$ were separated by a HPLC separation technique [162]. It was shown that for this ligand the σ-donor properties of the $N4$ site are weaker than for the $N1$ site. However, the difference is small, as can be seen from the pK_a values of the two sites obtained from UV–Vis absorption spectra. For $[Ru(bpy)_2(N4\text{-}Pytrz)]^+$ and $[Ru(bpy)_2(N2\text{-}Pytrz)]^+$ values of 5.95 and 4.07, respectively, were found. The same effect was found for the analogous pyrazin-2-yl (Pz) complexes: pK_a values of $[Ru(bpy)_2(N4\text{-}Pztrz)]^+$ and

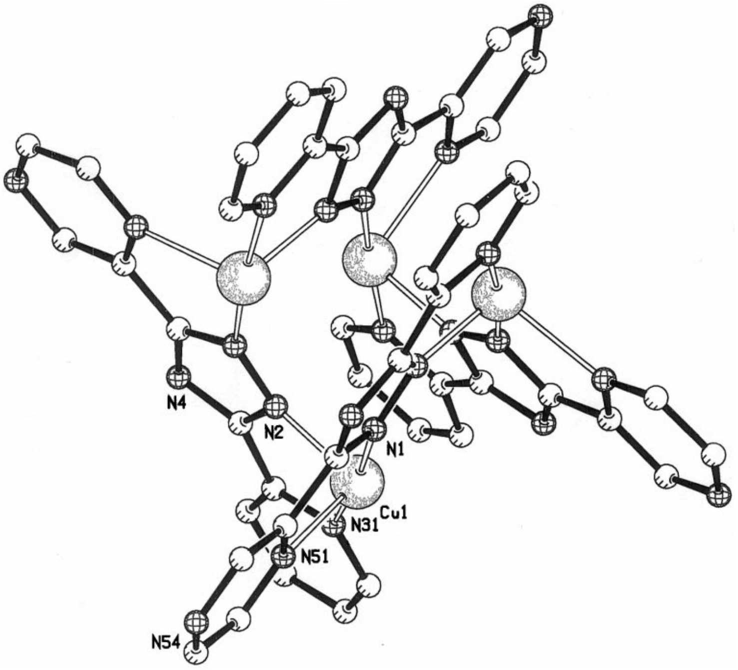

Fig. 22. Schematic representation of the tetranuclear cation of $[Cu_4(ppt)_4(H_2O)_4](NO_3)_4 \cdot 12H_2O$ [159].

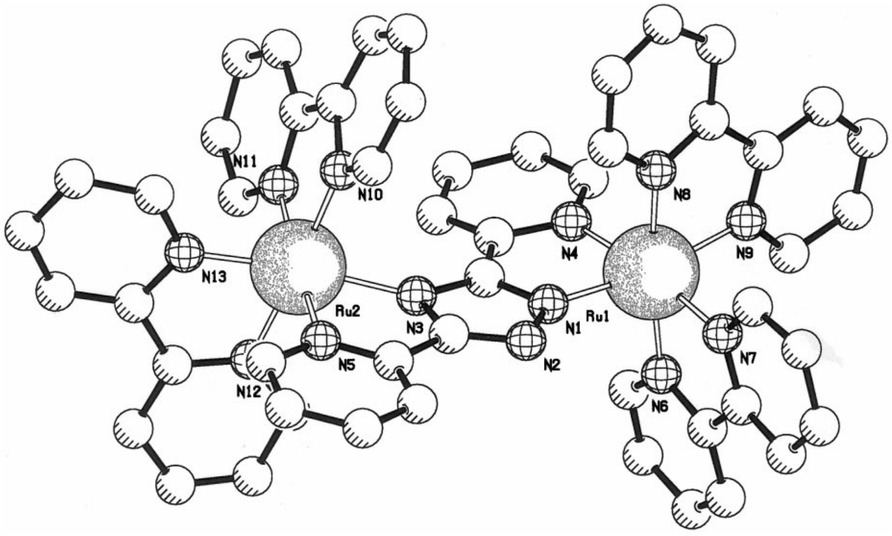

Fig. 23. Cation $[Ru(bpy)_2(35Py_2trz)Ru(bpy)_2]^{3+}$ showing the asymmetric triazole bridge [37].

$[Ru(bpy)_2(N2\text{-}Pztrz)]^+$ are 5.3 and 3.7, respectively. Therefore, predicting the preferred donor atom, imino or hydrazinic, is hardly possible as one has to include energy effects as hydrogen bonding, stacking and π-donor/acceptor properties in addition to the difference in σ-donor properties of the two sites.

Dinuclear compounds with the 'long' bridging mode are still few in number and only found for triazoles with chelating substituents. Examples are compounds of the general formula $[M(bpy)_2(3,5\text{-}R_2trz)M'(bpy)_2]^{3+}$, in which M and M′ are Ru, Os, Rh and/or Ir and R is pyridin-2-yl, pyrazin-2-yl and bpy replaced by phenylpyridine for Rh or Ir (see Fig. 23).

These dinuclear complexes possess a unique asymmetry by the bridging 3,5-Pytrz anion with two slightly different N-donor atoms, which allows the syntheses of isomeric heterodinuclear species, each having different electrochemical and electronic properties. Due to strong σ-donating and weak π-accepting properties of the bridge, the LUMO is located here on the auxiliary bpy ligands. This is reflected in the reduction potentials and photophysical behaviour. Going from a mononuclear to a dinuclear species, the negative charge on the bridge has to be shared by two metal ions and consequently the electron density on each metal ion diminishes, causing a blue shift of the absorption and emission MLCT bands and higher 1st oxidation potentials for the dinuclear complexes. A further point of interest is the great extent of electron delocalization and efficient energy-transfer processes for the dinuclear mixed-valence complexes. This strong interaction is caused by efficient mixing of high-lying occupied orbitals of the ligand and the dπ orbitals of the metal ions.

The behaviour of chelating triazoles towards first row transition elements, especially copper, has been investigated by Van Koningsbruggen. A series of dinuclear copper(II) complexes were prepared with 3-pyridyltriazole [163], only one chelate ring is involved in the coordination to copper. As a result, the double *N*1,*N*2 bridge becomes asymmetric with Cu–N–N angles of about 126 and 140°. An empirical relation between the magnetic interaction parameter of the copper(II) ions and the Cu–N–N angle was found [32,164]. Other ligands involved in this investigation were 4-amino-3,5-bis(aminomethyl)-1,2,4-triazole (aamt) and 4-amino-3,5-bis(*N*-methylaminomethyl)-1,2,4-triazole (maamt).

Interesting stacking interactions were observed in the mixed-valence tetranuclear copper complexes with this ligand. In $[Cu_2(maamt)_2(CuX_3)_2]$ with $X = Cl$, Br the anions CuX_3^{2-} coordinate on the axial positions of a planar dinuclear copper complex, the Cu(I) centres stack to the triazole rings at a distance of 327 pm [165] (see Fig. 24).

Iron(II) complexes of 3-pyridyltriazoles were initially studied by Hage and Reiff [166,167]. A comprehensive study of the spin crossover properties of the iron(II) complexes with these and analogous ligands has been made by Sugiyarto and Goodwin. The ligands 2,6-bis(triazol-3-yl)pyridine, 2,6-bis(1-methyltriazol-3-yl)pyridine, 2,6-bis(5-methyltriazol-3-yl)pyridine and 2,6-bis(1,5-dimethyltriazol-3-yl)pyridine give $Fe(L)_2$ complexes. The complex with the 5-methyl derivative gives a gradual spin transition on cooling [168]. Methyl substituted 3-pyridyltriazoles appear to give spin crossover systems with several iron(II) salts [169]. T_cs were below r.t..

An interesting tridentate ligand is 2-(1,5-dimethyltriazol-3-yl)-1,10-phenanthroline [170]. With $Fe(ClO_4)_2$ two polymorphs of composition $[FeL_2](ClO_4)_2{\cdot}2/3H_2O$

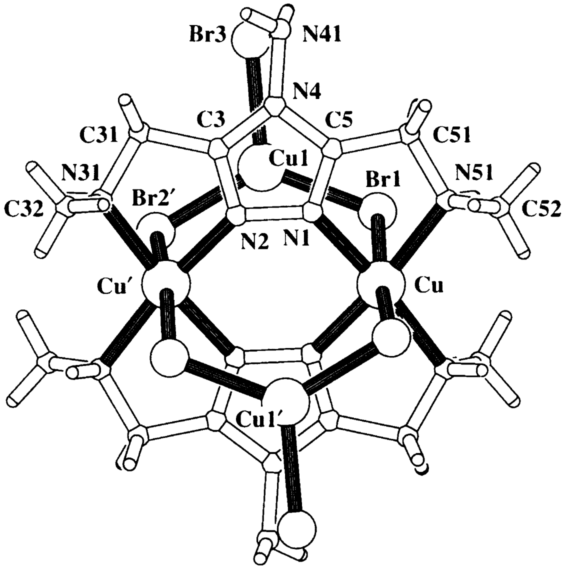

Fig. 24. Projection of the structure of $[Cu_2(maamt)_2(CuBr_3)_2]$ showing the stacking of $CuBr_3$ anions with triazole rings [32,165].

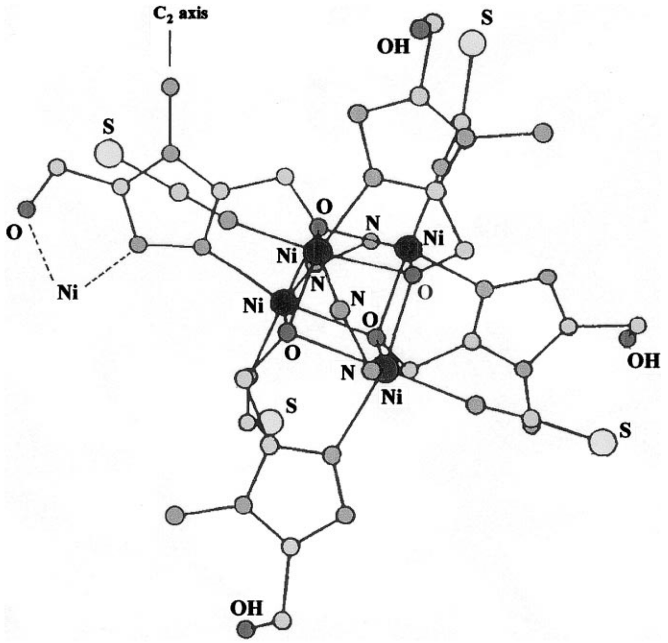

Fig. 25. Schematic drawing of one cubane cluster of the octanuclear double-cubane compound of composition $[\{Ni_4(H_2ahmt)_2(Hahmt)_3(NCS)_4\}_2(ahmt)]\cdot 12H_2O$[172]. The doubly deprotonated ligand ahmt is on the two-fold axis bridging two cubane clusters. Of the two neutral ligands H_2ahmt only the *N*1,*N*2 bridges are shown.

(**1**) and $[FeL_2](ClO_4)_2\cdot 2H_2O$ (**2**) were found. Polymorph **1** is at r.t. in the low spin state, whereas **2** is two thirds in the high spin state. Several other methyl derivatives were also studied [15].

The ligand 2,2′-bis(1-methyl-3-pyridyl-triazol-5-yl)biphenyl is capable of wrapping itself around Cu(I) or Cu(II). Two X-ray structures of this kind have been published [171].

7.2. *O-donors in chelating substituents*

Of particular importance for the stabilisation of the structure are the hydrogen bonds in the cubane type clusters of nickel(II) and 4-amino-3,5-bis(hydroxymethyl)triazole. Tetranuclear and octanuclear complexes were found [172] (see Fig. 25).

Compounds in which the three metal ions are arranged according to the corners of a more or less regular triangle are also rather well known for single *N*1,*N*2 bridging triazoles with a chelating substituent on the 3-position. Often a central OH ligand assists in the stabilisation of the structure by coordination to all three metal atoms. This has the effect of a pyramidal distortion on the structure, like in a complex of copper(II) nitrate and 3-(2′-hydroxyphenyl)-4-phenyltriazole) [120] (see Fig. 26).

A special, as yet unique case is a copper complex of triazole 3,5-dicarboxylic acid (H_3tdca); the structure of [[$Cu_3(tdca)_2(dien)(H_2O)_2 \cdot 3H_2O]_\infty$] is a chain of two sub-chains each built up from trinuclear units [173] (see Fig. 27).

Triazoles can also be combined with nitroxyl radical substituents. The structure of [Cu(4Me3Nittrz)$_4$](ClO_4)$_2$ was solved and the magnetic properties of the 11/2 spin system were analysed in detail [174].

Of course a five-membered chelate ring of which a triazole N is one of the donor atoms, distorts the in-plane geometry around the metal by elongation of bonds and deviation of the angles from 90°. This effect is distinctly smaller when the chelate ring is a six-membered ring. Several compounds with 3-acetylaminotriazole as the ligand have been studied [175,176].

A genuine pentanuclear copper(I) complex with a large macrocyclic ligand (ML) is [Cu_5(ML)$_2$(35Me$_2$trz)$_2$](ClO_4)$_3 \cdot 1.7C_2H_5OH$. This compound again shows the great potential for the combination of chelating ligands with relatively simple triazoles as linking blocks in the synthesis of high nuclearity coordination compounds. Two more pentanuclear Cu^+ compounds with similar structure were described in the same paper [177].

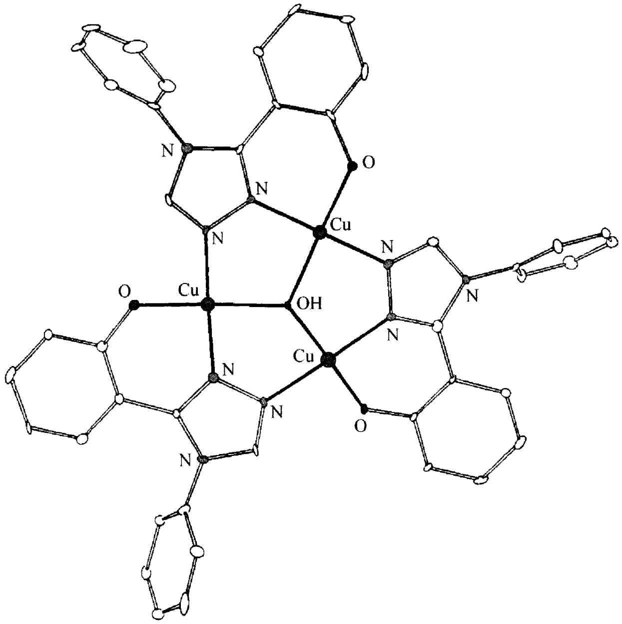

Fig. 26. Schematic structure of [$Cu_3(OH)(hppt)_3(NO_3)_2] \cdot 4H_2O$, the trinuclear units are linked to pairs by bridging nitrates [120].

8. 1,2,4-Triazoles as part of condensed ring systems

1,2,4-Triazoles can often occur in condensed multi-ring systems. Of these systems only [1,2,4] triazolo[1,5-*a*]pyrimidine has been investigated extensively. These ligands are studied because of their similarity to nucleic bases in reactions with metal ions.

The [1,2,3]triazolo[1,5-*a*]pyrimidine ligand has three potential donor atoms, *N*1, *N*3 and *N*4. Because these sites are all different a number of different coordination modes is possible: three monodentate and three didentate modes and one tridentate mode. The preferred metal binding site is *N*3 in the monodentate mode. This is also the case in didentate coordination, together with either *N*1 or *N*4, or with *N*1 *and* *N*4 in tridentate coordination. So *N*3 is always involved in the coordination. There seems to be only one exception: *N*1 coordination in $[HgCl_2(Hmpto)]_2 \cdot Hmpto \cdot H_2O$ [178]. For steric reasons none of these oligodentate modes can give chelate rings with the metal ions, all are oligonucleating modes.

Ligands studied in this group are unsubstituted [1,2,4]triazolo[1,5-*a*]pyrimidine (tp), 5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidine (5mtp), 6-methyl[1,2,4]triazolo[1,5-*a*]pyrimidine (6mtp), 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine (dmtp), 4,7-dihydro-5-methyl-7oxo[1,2,4]triazolo[1,5-*a*]pyrimidine (Hmtpo), 4,7-dihydro-4,5-dimethyl-7-oxo[1,2,4]triazolo[1,5-*a*]pyrimidine (dmtpo) 5,7-diphenyl[1,2,4]triazolo-[1,5-*a*]pyrimidine (dptp), 6,8-dimethyl[1,2,4]triazolo[3,4-*b*]pyridazine (dmtpz) and [1,2,4]triazolo[1,5-a]pyridine (tpy).

The unsubstituted tp ligand is the *N*3 donor in tetrahedral $Zn(tp)_2Br_2 \cdot 1/2H_2O$[179] and in the compressed trigonal-bipyramidal $Cu(tp)_2(H_2O)Br_2$ [180]. This ligand is *N*1,*N*3 didentate in an X-ray isomorphous series of $M(tp)_2(NCS)_2$ with M = Mn, Fe, Co, Ni, of which the structure of the iron compound has been solved [36] (see Fig. 28). The ligand shows here the same bridging coordination as in the thiocyanate complexes with the unsubstituted triazole resulting in a 2d-layer structure, described above [33]. With copper in $Cu(tp)_2(NCS)_2$ and $Cu(tp)_2Cl_2$ the same coordination mode was found, albeit with the *N*1 in semi-coordination to copper [181]

Compounds with 5mtp comprise $M(5mtp)_2(H_2O)_2(NCS)_2$ with M = Fe [182] and Co [183]. In both cases 5mtp coordinates through *N*3. $Cu(5mtp)_2(NCS)_2$ [184] shows the *N*1,*N*3 mode, again with *N*1 in semi-coordination on the elongated axis to copper(II). The ligand 6mtp, however, in a complex of the same composition, $Cu(6mtp)_2(NCS)_2$ has only *N*3 coordination [184].

The extensively studied ligand dmtp coordinates in almost all cases through *N*3. Among the first examples is an X-ray isomorphous series of composition $M(dmtp)_2(H_2O)_2(NCS)_2$ with M = Mn, Fe, Co, Ni, Cd, of which the structure of the cadmium complex was determined [185]. Several complexes with $[Hg(SCN)_4]$ as the bridging group to first-row transition metals coordinated further by water, and variable numbers of dmtp have been described [186–188].

Ligands with pronounced monodentate properties like these triazolopyrimidines may of course be involved in oligonuclear complexes formed by other bridging groups. Examples are the two isomers of $[Cu_2(dmtp)_4(NCS)_4]$ [189,190]. The

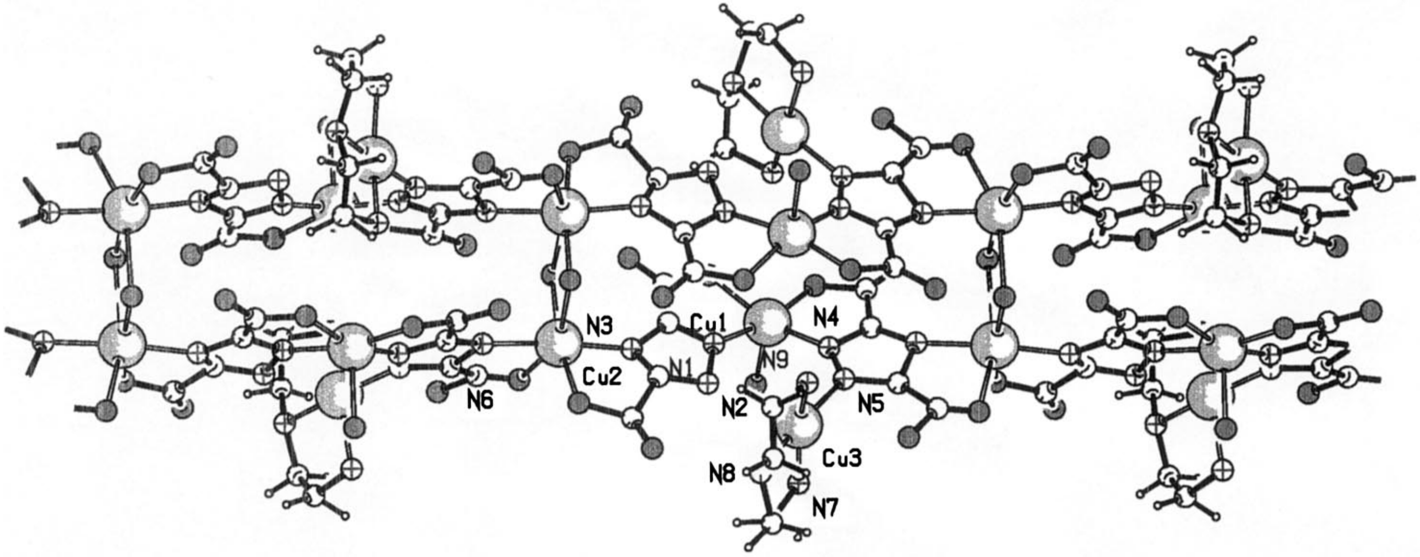

Fig. 27. Representation of the chain structure of $[Cu_3(tdca)_2(dien)(H_2O)_2{\cdot}3H_2O]_\infty$, H_3tdca = triazole-3,5-dicarboxylic acid [173].

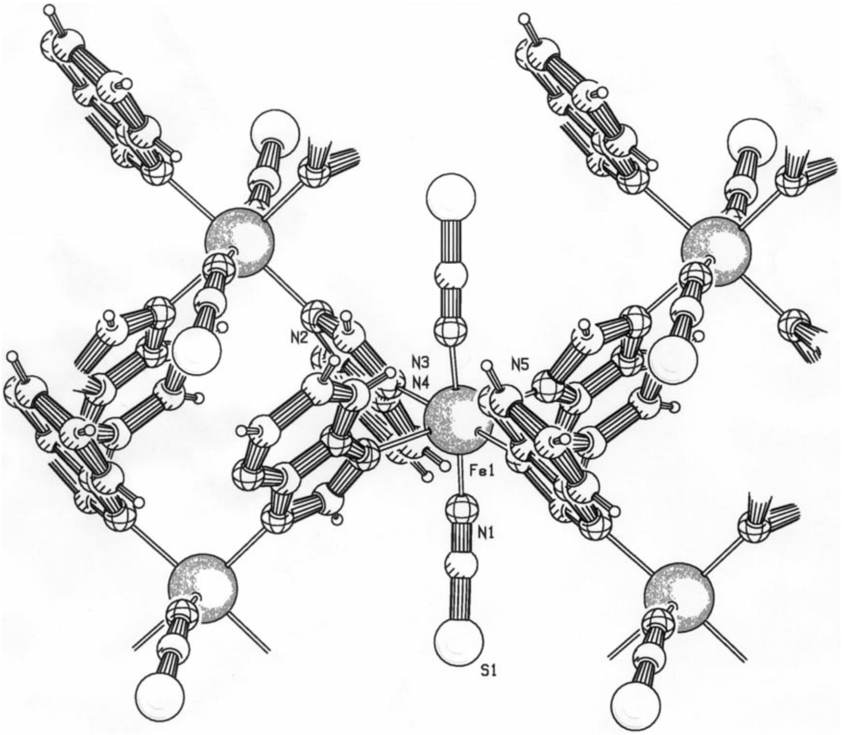

Fig. 28. Coordination around the iron of the layer structure of [Fe(tp)$_2$(NCS)$_2$] [36].

difference between the two isomers is in the coordination of the bridging NCS. The α isomer has the sulfur atom at the apical position of a distorted square pyramid around copper, whereas in the β isomer it is the nitrogen on the apical position and the sulfur equatorial. As both coordination geometries are not purely square pyramidal, this isomerism was termed distortion isomerism (see Fig. 29).

Exceptions in the uniformity of *N*3 coordination for dmtp are found with Cu(I) and Ag(I): [Cu$_4$(dmtp)$_4$Cl$_2$][Cu$_2$Cl$_4$] [191], [Ag$_2$(dmtp)$_2$(NO$_3$)$_2$] [192], [Ag$_2$(dmtp)$_2$-(HSO$_4$)$_2$]·4H$_2$O and [Ag$_2$(dmtp)$_2$SO$_4$][Ag$_2$(dmtp)$_2$(HSO$_4$)$_2$]·H$_2$O [193].

In the copper compound the ligand bridges through *N*3,*N*4 in a tetranuclear cation. Two sets of two metal ions are bridged by two ligands in a plane (Fig. 30). Stacking interactions of the condensed aromatic rings are important in the stabilisation of this structure.

In the second compound a similar *N*3,*N*4 bridge with two silver atoms and two dmtp ligands is formed. The difference between the two bridges is that the Cu$_2$(dmtp)$_2$ bridge has a mirror plane, whereas the Ag$_2$(dmtp)$_2$ unit has an inversion centre between the silver atoms. Both type of bridges occur in the silver sulfate complexes [193].

The dmtp ligand may form coordination compounds with almost any metal. Stabilizing factors are the formation of hydrogen bonds [194] through non-coordination nitrogen donors and the tendency towards stacking of the condensed aromatic ring systems [195]. Recently, a $RuCl_3$ complex with dmtp was studied in a research programme towards ruthenium based anti-tumour drugs [196] (see Fig. 31).

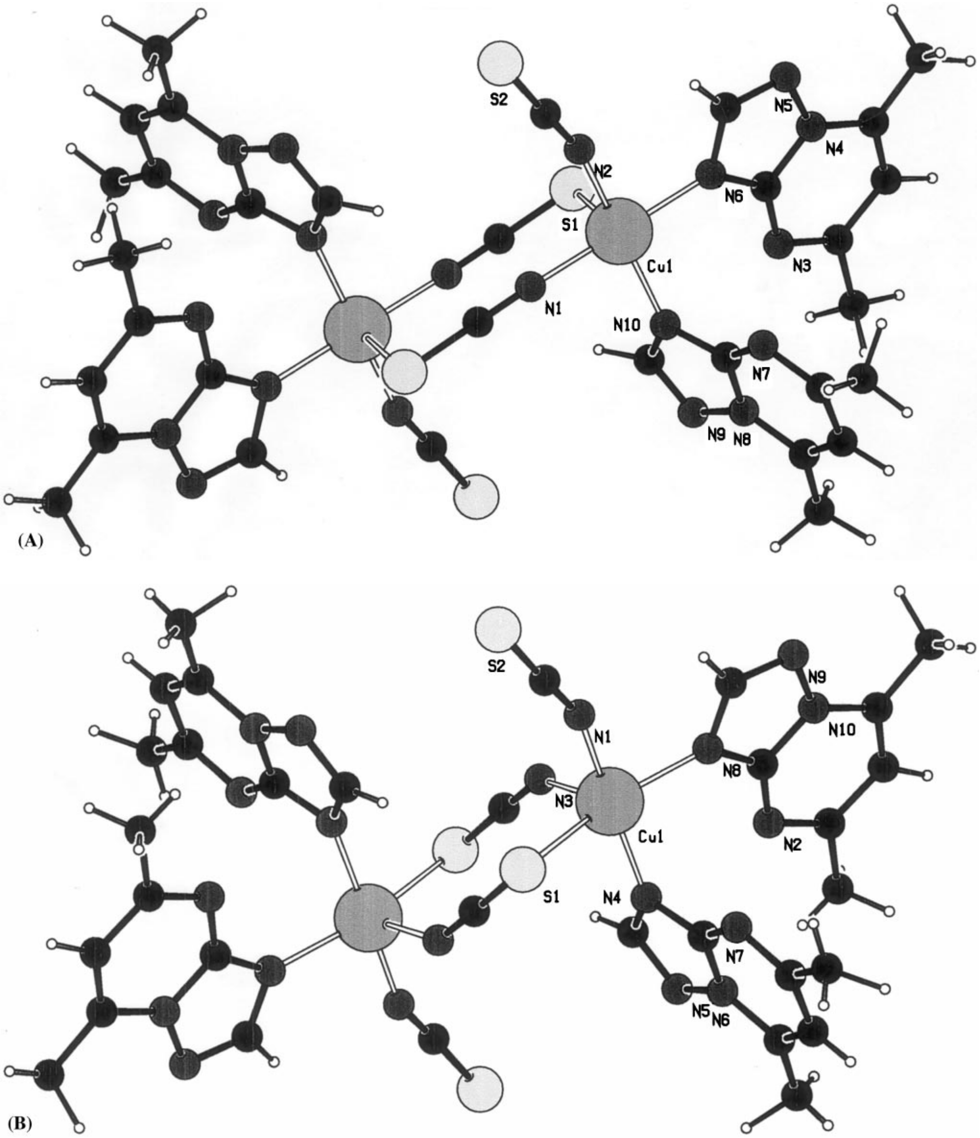

Fig. 29. Distortion isomerism in $[Cu_2(dmtp)_2(NCS)_4]$: (A) α isomer with sulfur as apex; (B) β isomer with nitrogen as apex [190].

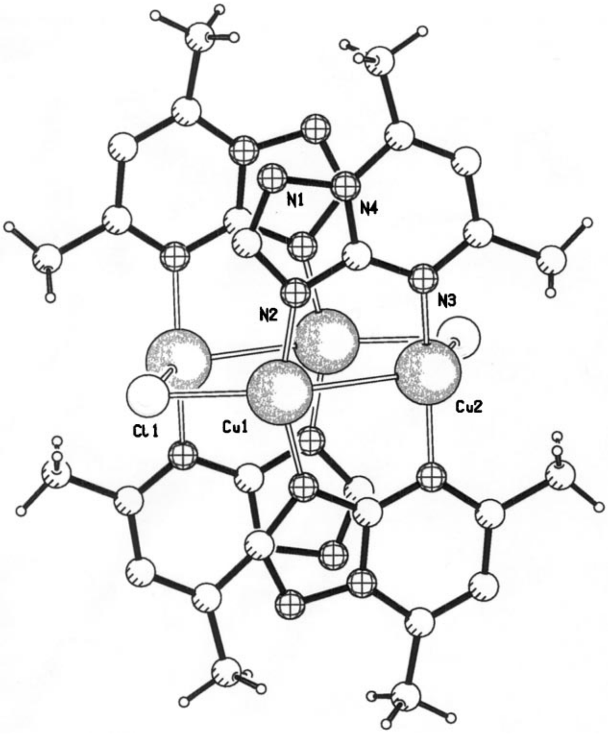

Fig. 30. Cation of $[Cu_4(dmtp)_4Cl_2](Cu_2Cl_4)$ showing chloride bridges, *N*3,*N*4 bridges of dmtp and the stacking arrangement of the dmtp ligands [191].

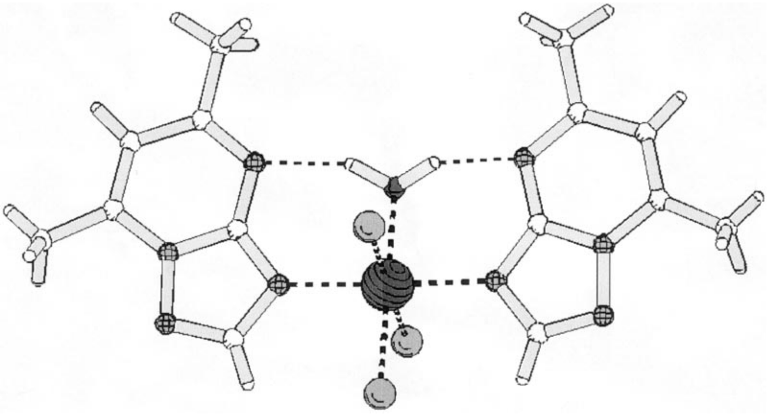

Fig. 31. Drawing of the structure of $[Ru(dmtp)_2(H_2O)Cl_3]$ showing the double hydrogen bond from coordinated the water ligand [196].

A likewise versatile ligand with the same ring system is 4,7-dihydro-5-methyl-7-oxo[1,2,4]triazolo[1,5-*a*]pyrimidine (Hmtpo). This ligand, more specifically its anion, has in addition to four potentially donating nitrogen atoms an oxygen on position 7 with which it can form a chelate bridge together with *N*1. All donor sites were used in [Ag(mpto)] whose structure [197] was already published in 1976. The usual *N*3 again is donor in $[Cu(H_2O)_4(mtpo)_2]$ and $[Cu(NH_3)_2(H_2O)_2(mtpo)_2]$ [198] and most probably also in a series of first row transition metal (and cadmium) complexes of composition $[MX_2(Hmtpo)_2]$ M = Mn, Fe, Co, Ni, Cu, Cd and X = Cl, Br. The syntheses and spectral properties of these compounds were discussed on the basis of *N*3 coordination [199]. The coordination of Hmpto and $mpto^-$ to heavy transition metals (Ag, Pd, Pt, Hg) has been recently explored. In these compounds, in addition to *N*3 coordination, the ligand is often found in the bridging *N*3,*N*4 mode. In one case, $[Hg(Hmpto)Cl_2]_2 \cdot Hmpto \cdot H_2O$, it is *N*1 monodentate [178].

Less developed is the coordination chemistry of the [1,2,4]triazolo[3,4-*b*]pyridazine ring system. The dimethyl derivative, 6,8-dimethyl[1,2,42]triazolo[3,4-*b*]pyridazine (dmtpz), can be synthesized as easily as dmtp. A chain structure with cadmium thiocyanate has been published: $[Cd(dmtpz)_2(NCS)_2]$ [200]. This ligand is further studied for potential anti-tumour properties in combination with ruthenium [196].

9. Historic overview of structures of coordination compounds of 1,2,4-triazoles

Compounds listed in Table 1 are those for which the structure is known from single-crystal X-ray diffraction.

Compounds have been listed in chronological order of publication. The list of compounds serves both as an overview of the published structures and as an entry to the literature of these complexes as a group. As an overview of metal triazole complexes the list is not a complete one, as many combinations of triazoles and metal salts have been described, both in scientific journals and in the patent literature, without any investigation on the composition or structure. However, the list is complete for X-ray structures published up to spring 1999 and available in the CSD.

10. Conclusion and outlook

Metal coordination compounds of the 1,2,4-triazoles appear to possess a great diversity of structures. This diversity is strongly connected to the di- and trinucleating properties of the neutral and, respectively, anionic triazole ring.

Research on these complexes continues to grow. Triazoles have been investigated intensively over the years for pharmaceutic purposes. Although triazoles are mainly non-natural chemicals, their geometry makes them suitable for mimicking the natural imidazoles. It is very likely that triazole–metal interactions play a major role in the biological actions of triazole-containing drugs and agricultural chemicals. In addition to these, a number of other applications have been claimed for metal–triazole compounds. These include applications as anti-corrosion coatings, photographic materials, dyes, complexing agents for spectrophotometric determination of metal ions and additives for oils and greases. New applications are in the field of medicine [196,272] and chelating polymers [273,274]. The use of triazoles in the metal anti-tumor drug research has only just started.

To understand these interactions of triazoles with metals, as for example in the above-mentioned anti-corrosion coatings, further research on the geometry of triazole–metal compounds is of great necessity. A new area is the search for triazole ligands to be used in iron(II) spin crossover systems. This area is also rapidly evolving. Further, the application of triazoles in ferromagnetic materials is a subject of study.Many more structural features will certainly be discovered in the near future. In particular more structural information concerning the one-dimensional polynuclear complexes with triple triazole bridges between the metal ions will be of great value.

11. Supplementary material

Copies of the Leiden theses are available from the author on request.

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Appendix A. List of abbreviations

Systematics

Amino groups are abbreviated by lower case *a*, alkyl and aryl substituents are abbreviated by their common abbreviations Me, Et, Pr, Ph,…preceded by their locant number and followed by trz for the triazole ring. Active hydrogen on any nitrogen of the triazole ring is indicated by H, loss of this hydrogen gives the triazolate anion. Examples: 4-amino-1,2,4-triazole is abbreviated as 4atrz, 3-methyl-1,2,4-triazole becomes 3Metrz and 3,5-diamino-1,2,4-triazole $35a_2Htrz$, its anion: $35a_2trz$.Several compounds, especially those with complex substituents, are abbreviated with a non-systematic abbreviation.

a	amino
35a$_2$Htrz	3,5-diamino-1,2,4-triazole
aamt	4-amino-3,5-bis(aminomethyl)-1,2,4-triazole
aat	3-acetylamino-1,2,4-triazole
admtp	2-amino-5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine
4Altrz	4-allyl-1,2,4-triazole
4atrz	4-amino-1,2,4-triazole
attn	1,9-bis(3-aminotriazol-5-yl)-3,7-dithianonane
bmptb	2,2′-bis(1-methyl-3-pyridyltriazolyl)biphenyl
bpy	2,2′-bipyridine
4,4′-bpy	4,4′-bipyridine
btb	1,4-bis(triazol-1-yl)butane
bte	1,2-bis(triazol-1-yl)ethane
btp	1,3-bis(triazol-1-yl)propane
btpy	2,6-bis(1,2,4-triazol-3-yl)pyridine
btr	4,4′-bitriazole
btx	1,6-bis(triazol-1-yl)hexane
4^{t}Butrz	4-*tert*-butyl-1,2,4-triazole
3CF$_3$5SH4atrz	4-amino-3-(trifluoromethyl)-1,2,4-triazol-5-thiol
4^{p}CH$_3$Otrz	4-(*p*-methoxyphenyl)-1,2,4-triazole
cod	cyclooctadiene
dien	1,5-diamino-3-azapentane
dmtb	3,3-dimethyl-1-(triazol-1′-yl)-2-butanone
dmtp	5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine
dmtph	2-(1,5-dimethyltriazol-3-yl)-1,10-phenanthroline
dmtpz	6,8-dimethyl[1,2,4]triazolo[3,4-*b*]pyridazine
dppm	bis(diphenylphosphinomethane)
dppt	3,5-dipyridyl-4-(pyrrol-1-yl)-1,2,4-triazole
dptp	5,7-diphenyl[1,2,4]triazolo[1,5-*a*]pyrimidine
en	1,2-diaminoethane
35Et$_2$Htrz	3,5-diethyl-1,2,4-triazole
1Ettrz	1-ethyl-1,2,4-triazole
4Ettrz	4-ethyl-1,2,4-triazole
H$_2$ahmt	4-amino-3,5-bishydroxymethyl-1,2,4-triazole
Hbatt	1,3-bis(5-aminotriazol-3-yl)triazene
H$_2$dabt	5,5′-diamino-3,3′-bis-1,2,4-triazole
Hhppt	3-(2′-hydroxyphenyl)-4-phenyl-1,2,4-triazole
H$_2$hppyt	3-(2′-hydroxyphenyl)-5-(pyridin-2-yl)-1,2,4-triazole
Hmtpo	7-hydroxy-5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidine
4HOEttrz	4-(2-hydroxyethyl)-1,2,4-triazole
Hpz	pyrazole
H$_3$tdca	1,2,4-triazole-3,5-dicarbonic acid
Htrz	1,2,4-triazole
maamt	4-amino-3,5-bis(methylaminomethyl)-1,2,4-triazole
3Me4atrz	4-amino-3-methyl-1,2,4-triazole

35Me$_2$4atrz	4-amino-3,5-dimethyl-1,2,4-triazole
3Me4^{t}Butrz	4-*tert*-butyl-3-methyl-1,2,4-triazole
3Me4Ettrz	4-ethyl-3-methyl-1,2,4-triazole
35Me$_2$Htrz	3,5-dimethyl-1,2,4-triazole
1Meiz	1-methylimidazole
4Me3Nittrz	2-(4-methyltriazol-3-yl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide
4Me$_2$Ntrz	4-(dimethylamino)-1,2,4-triazole
4Metrz	4-methyl-1,2,4-triazole
345Me$_3$trz	3,4,5-trimethyl-1,2,4-triazole
3Me$_4$Phtrz	3-methyl-4-phenyl-1,2,4-triazole
3Me$_5$PyHtrz	3-methyl-5-(pyridin-2′-yl)-1,2,4-triazole
1Me$_3$Pytrz	1-methyl-3-(pyridin-2′-yl)-1,2,4-triazole
3Me$_1$Pytrz	3-methyl-1-(pyridin-2′-yl)-1,2,4-triazole
4Me$_3$Pytrz	4-methyl-3-(pyridin-2′-yl)-1,2,4-triazole
15Me$_2$3Pytrz	1,5-dimethyl-3-(pyridin-2′-yl)-1,2,4-triazole
3Me$_5$SH$_4$atrz	4-amino-3-methyl-1,2,4-triazole-5-thiol
5mtp	5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidine
6mtp	6-methyl[1,2,4]triazolo[1,5-*a*]pyrimidine
1mtph	2-(1-methyltriazol-3-yl)-1,10-phenanthroline
5mtph	2-(5-methyltriazol-3-yl)-1,10-phenanthroline
4Phtrz	4-phenyl-1,2,4-triazole
ppt	3-(pyridin-2-yl)-5-(pyridazin-2-yl)-1,2,4,-triazole
ppy	pyridin-2-yl-2′-phenylato anionic ligand
4^{i}Prtrz	4-isopropyl-1,2,4-triazole
Py	pyridin-2-yl
35Py$_2$4atrz	4-amino-3,5-bis(pyridin-2′-yl)-1,2,4-triazole
3PyHtrz	3-(pyridin-2′-yl)-1,2,4-triazole
35Py$_2$Htrz	3,5-bis(pyridin-2′-yl)-1,2,4-triazole
Pz	pyrazin-2-yl
satz	4-salicylideneamino-3,5-dimethyl-1,2,4-triazole
5SH$_4$atrz	4-amino-1,2,4-triazol-5-thiol
tbima	tris((benzimidazol-2-yl)methyl)amine
TCNQ	7,7,8,8-tetracyanoquinodimethane
tfb	5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene
4-*p*-Toltrz	4-*p*-tolyl-1,2,4-triazole
tp	[1,2,4]triazolo[1,5-*a*]pyrimidine
trz	1,2,4-triazolate(1−) ion or 1,2,4-triazole nucleus as part of an abbreviation

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