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Metal complexes of [1,2,4]triazolo-[1,5-a]pyrimidine derivatives

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Contents

Abstract

This article covers all the research work published until September 1998 about the coordination chemistry of 1,2,4-triazolo-[1,5-a]pyrimidine derivatives. The revision is mainly focused in the structural features of the compounds, obtained from single crystal X-ray diffraction. The references are classified according to the present metal atoms. These kind of ligands display a broad versatility when binding metal ions, monodentate binding through

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the endocyclic nitrogen atom at position 3 being however their main coordinating behaviour. Dimeric and polymeric structures are observed when a bidentate binding through N3–N4 or N3–N1, respectively, takes place. N1–O7 chelating binding mode has also been observed in a few cases. In some cases, dimers or polymers are also generated when the present auxiliary ligands are the ones that bridge the metal centres.

Keywords: Triazolopyrimidines; Metal complexes of triazolopyrimidines; Purine analogs; X-ray structures

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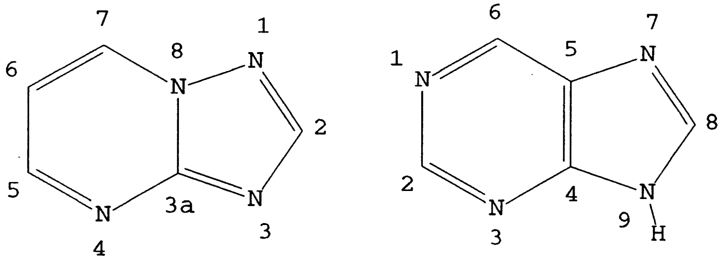
1. Introduction

The chemistry of 1,2,4-triazolo-[1,5-a]pyrimidine derivatives started in 1909 when Bulow and Haas [1] reported the synthesis of several of these compounds. The use of 4,7-dihydro-5-methyl-7-oxo-1,2,4-triazolo-[1,5-a] pyrimidine (HmtpO) as stabilizer of photographic emulsions was discovered in 1935 by Birr [2] whose subsequent extensive physicochemical studies led to a plausible theory of its role in the emulsions [3,4]. Since then, other 1,2,4-triazolo-[1,5-a]pyrimidine derivatives have found uses in different areas such as pharmaceutical and agricultural applications; for example, 7-(*N*,*N*-diethylamine)-5-methyl-1,2,4-triazolo-[1,5-a]pyrimidine is clinically used as a coronary dilator [5] and several 1,2,4-triazolo-[1,5-a]pyrimidine-2-sulfonamides act as active herbicides for the control of broad leaf weeds in cereal crops [6,7].

The basic skeleton of 1,2,4-triazolo-[1,5-a]pyrimidines differs from the purine ring in having a pyrimidine nitrogen atom in a bridgehead position with disappearance of the acidic H-proton of the five-membered ring. The scheme below compares these two bicyclic systems, depicting the IUPAC numbering scheme used for the triazolopyrimidine derivatives (and used throughout this article) and the biochemical numbering scheme, more usually used for purines.



Because of the similarity of both systems, coordination compounds of 1,2,4-triazolo-[1,5-a]pyrimidines can be considered as model systems for various naturally occurring metal coordination compounds. Thus, compounds bidentately coordinated through N3 and N4 positions can act as model systems for adenine. Likewise, the triazolo ring has a geometry and an electronic structure similar to that of imidazole and therefore, when bridging through N1 and N3, the 1,2,4-triazolo-[1,5-a]pyrimidines are specially suited for mimicking imidazolato bridges in model compounds for metalloproteins such as superoxidodismutase [8].

1,2,4-triazolo-[1,5-a]pyrimidine derivatives are ligands that display a great versatility in their interactions with metal ions, not only because they can bind the metal atom through different positions, as will be shown throughout this review, but also because their presence influence the behaviour of other auxiliary ligands, either by electronic or steric reasons, giving rise in some cases to compounds with interesting metal–metal interactions through these auxiliary ligands [9].

Until now, the study of the interactions of metal ions with these ligands has been mainly focused on those that are commercially available: unsubstituted 1,2,4-triazolo-[1,5-a]pyrimidine (tp), its derivative methylated at positions 5 and 7 (dmtp) and that with a methyl group at position 5 and an oxo group at position 7 (HmtpO), with few references to other derivatives [10,11].

This review focuses on the results obtained in the synthesis, spectroscopic properties, structural characterization (mainly by X-ray diffraction) and biological activity of metal complexes of 1,2,4-triazolo-[1,5-a]pyrimidine derivatives. Most of the work presented here is contribution of two research groups: one in Italy and The Netherlands and the other, ours at the University of Granada. The program XP, included in the SHELXTL PLUS package [12] has been used for drawing the crystallographic figures, the corresponding coordinates having been obtained via the Cambridge Structural Database [13].

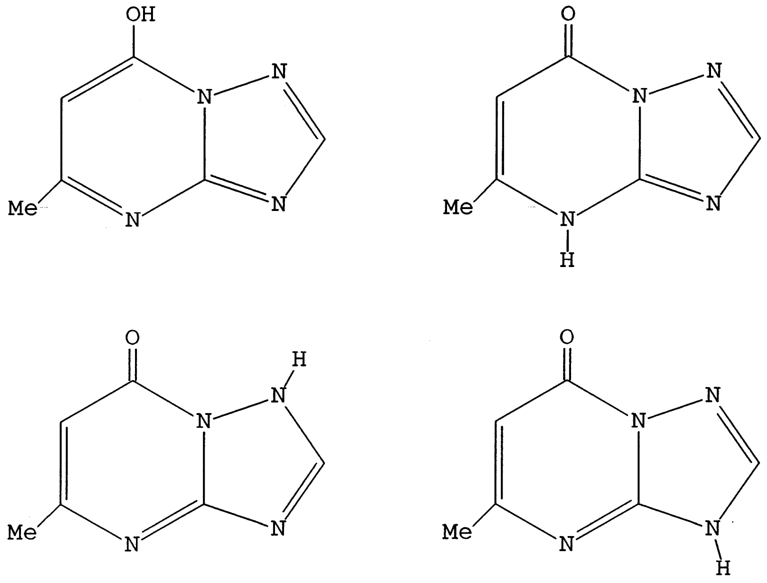


Fig. 1. Possible tautomeric forms for HmtpO.

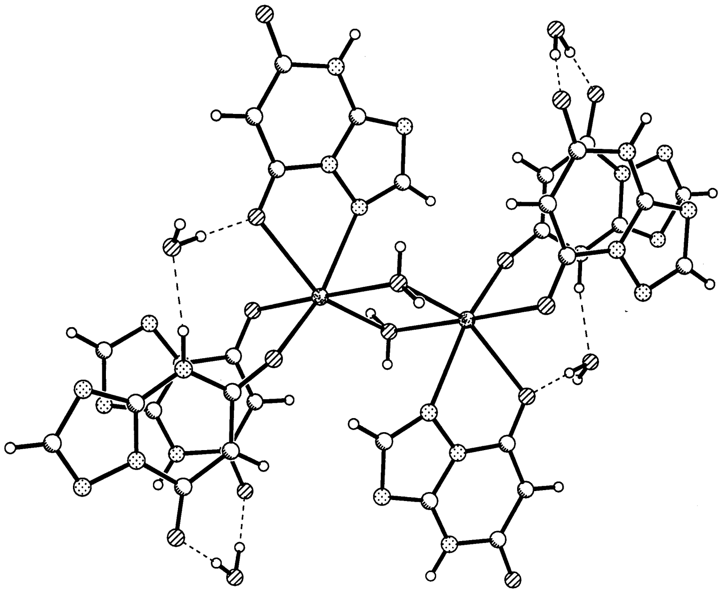


Fig. 2. Environment of two sodium atoms in the crystal structure of $Na(HtpO_2)\cdot 2H_2O$. Adapted from Orihuela et al. [26].

2. The ligands

Many references about the synthesis of 1,2,4-triazolo-[1,5-a]pyrimidine derivatives are available [14–17] and an early revision was made by Mosbey [18] in 1961. Nevertheless, the most complete recent revisions on this subject are those by Fisher [19,20]. In these, it is shown that most syntheses of this type of compounds start either from a 1,2,4-triazole derivative or from a pyrimidine residue and need annulation of a second heterocyclic ring. 5-amino-1,2,4-triazole and 2-hydrazinopyrimidine are the most usual starting synthons. According to the reaction types these syntheses may be classified as cyclocondensations, cycloaditions or oxidative cyclizations. In some cases, the kinetically favoured [4,3-a] product is formed initially, this being transformed into the thermodynamically more stable [1,5-a] isomer by means of the Dimroth rearrangement [21].

1,2,4-triazolo-[1,5-a]pyrimidine derivatives with oxo substituents can exist in a number of tautomeric forms depending on the position the subsequent acidic proton is attached to. As an example, 4,7-dihydro-5-methyl-7-oxo-1,2,4-triazolo[1,5-a]pyrimidine (HmtpO) may exist in a lactim or three lactam forms (see Fig. 1). From ^{13}C-NMR data it was impossible to decide between the lactam forms supporting the hydrogen atom on N4 or N3 whereas ^{15}N-NMR proved that both tautomers are at equilibrium, which is fast on the NMR time scale

Table 1
Geometrical parameters in Cu(II) complexes

Compound	Equatorial atoms[a]	Axial atoms[a]	Cu–N3/Å	Cu–N1/Å	Ref.
$[Cu(NCS)_2(6mtp)_2]$[b]	N3,N3,Nt,Nt	–	1.975(2)	–	[10]
$[CuBr_2(tp)_2(H_2O)]$[c]	Br,Br,Ow	N3,N3[c]	1.969(3)	–	[38]
$[Cu(dmtp)_4(H_2O)_2](PF_6)_2$	N3,N3,N3,N3	Ow,Ow	2.019(3) 2.050(3)	–	[40]
$[Cu(mtpO)_2(NH_3)_2(H_2O)_2]$	N3,N3,Na,Na	Ow,Ow	2.016(3)	–	[41]
$[Cu(mtpO)_2(H_2O)_4]$	N3,N3,Ow,Ow	Ow,Ow	1.962(2)	–	[41]
$[Cu(dmtp)_3(H_2O)_2](ClO_4)_2 \cdot 2H_2O$	N3,N3,N3,Ow	Ow	1.985(5) 1.993(4) 2.024(4)	–	[42]
$[Cu(mtpO)_2(en)_2]$	Na,Na,Na,Na	N3,N3	2.639(3)	–	[37]
$[Cu(mtpO)_2(en)(H_2O)] \cdot H_2O$	N3,N3,Na,Na	Ow	1.998(3) 2.010(3)		[24]
$[Cu(NO_3)_2(HmtpO)_2(H_2O)_2] \cdot 2H_2O$	N3,N3,Ow,Ow	On,On	1.988(3)	–	[24]
$[Cu(mtpO)_2(tn)] \cdot 2H_2O$	N3,O7,Na,Na	N1	1.987(3)	2.264(2)[d]	[24]
$[Cu(mtpO)_2(py)_2(H_2O)_2]$	N3,N3,Na,Na	Ow,Ow	2.027(4)	–	[24]
$[Cu(mtpO)_2(bpy)(H_2O)] \cdot EtOH \cdot H_2O$	N3,N3,Na,Na	Ow	1.950(8) 2.004(6)	–	[24]
$[Cu(mtpO)_2(phen)(H_2O)_2]$	N3,N3,Na,Na	Ow,Ow	2.011(3)	–	[24]
$[Cu(NCS)_2(5mtp)_2]$	N3,N3,Nt,Nt	N1,N1	2.020(4)	2.677(5)	[10]
$[CuCl_2(tp)_2]$	N3,N3,Cl,Cl	N1,N1	2.021(4)	2.692(4)	[43]
$[Cu(NCS)_2(tp)_2]$	N3,N3,Nt,Nt	N1,N1	2.035(5)	2.633(6)	[43]
$[Cu_2(5tpO)_4(H_2O)_2] \cdot 2H_2O$	N3,N3,N4,N4	Ow	1.985(9) 2.000(8)	2.036(7)[e] 2.080(9)[e]	[44]
$[Cu_2Br_4(dmtp)_2] \cdot 2H_2O$[c]	Br,Br,Br	N3,N3[c]	2.006(8) 2.012(7)	–	[39]
α-$[Cu_2(NCS)_4(dmtp)_4]$	N3,N3,Nt,Nt	St	2.000(7) 2.019(8)	–	[45]
β-$[Cu_2(NCS)_4(dmtp)_4]$	N3,N3,Nt,St	Nt	1.995(2) 2.058(2)	–	[46]
$[Cu_2(NCS)_4(HmtpO)_2(H_2O)_2]$	N3,Nt,Nt,St	Ow,St	2.074(2)	–	[9]

[a] Nt,St = N and S atoms of thiocyanate group. Na = N atom of ammonia or amine. Ow = O atom of water. On = O atom of nitrate group.

[b] Distorted tetrahedral geometry.

[c] Trigonal bipyramidal geometry; axial bonds are strong bonds.

[d] Cu–O7 distance = 2.109(2) Å.

[e] Cu–N4 distances.

[22]. The relative stabilities of these tautomers in the gaseous state and in solution may be estimated by means of ab initio and semiempirical calculations [23], these studies concluding that the most stable tautomer for HmtpO is the imino-ketone (lactam) form with the proton at N4 position. Analogous results have been obtained by our research group [24].

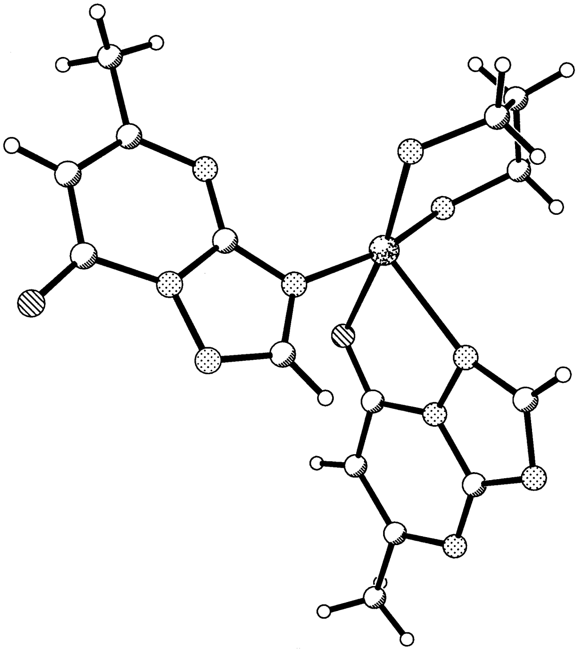


Fig. 3. Molecular structure of $[Cu(mtpO)_2(tn)] \cdot 2H_2O$. Adapted from Navarro et al. [24].

Another example is 4,5,6,7-tetrahydro-5,7-dioxo-1,2,4-triazolo-[1,5-a] pyrimidine (H_2tpO_2), with two acidic hydrogen atoms. Semiempirical molecular orbital calculations type RMF/AM1 [25] indicate that the most stable site for the most acidic proton is C6, generating in this way a strongly acidic active methylene group [26].

Crystallographic studies on 1,2,4-triazolo[1,5-a]pyrimidine derivatives are scanty, the first determination of a crystal structure of one of these compounds (4,7-dihydro-6-ethylcarbonyl-4-ethyl-7-oxo-1,2,4-triazolo-[1,5-a]pyrimidine) being performed as late as 1980 [27]. The crystal structure of HmtpO, for example, has not been solved until 1997 [28], displaying the expected N4–H tautomer with very strong N4–H...O7 hydrogen bonds that define a monodimensional polymer. On the other hand, the unexpected N3–H tautomer is present in the solid phase for 5-methyl-6-nitro-7-oxo-3,7-dihydro-1,2,4-triazolo[1,5-a]pyrimidine [29]. The monosodium salt of 4,5,6,7-tetrahydro-5,7-dioxo-1,2,4-triazolo-[1,5-a]pyrimidinate dihydrate ($NaHtpO_2 \cdot 2H_2O$) [26] displays the monoanionic form of H_2tpO_2, deprotonated at the active methylene group (C6) and keeping the hydrogen atom attached to N4; the metal atom is surrounded by five oxygen atoms and one nitrogen atom in a very distorted octahedral environment: N1 and O7 from one $HtpO_2^-$ anion, O7 from another, O5 from a third and two oxygen atoms from two crystallographically equivalent water molecules (Fig. 2). Recently, the crystal structures of 4,5-dihydro-5-oxo-1,2,4-triazolo[1,5-a]pyrimidine (5HtpO) and 4,7-dihydro-7-oxo-1,2,4-triazolo-[1,5-a]pyrimidine (7HtpO) have been solved by our research group [30].

3. Compounds without a direct metal-triazolopyrimidine bond

A few compounds have been described in which there is not a direct bond between the metal atom and the triazolopyrimidine derivative. Among these, there are examples with the organic molecule in neutral, cationic (protonated) and anionic form. Thus, three structures have been solved in which tetrakis(thiourea) palladium(II) chloride or tetrakis(thiourea)platinum(II) chloride cocrystallize with dmtp [31] or HmtpO [32]. In the cases of $[Ni(dmtp)_4(H_2O)_2](I_3)_2 \cdot (dmtp)_2$ [33] and $[HgCl_2(HmtpO)]_2 \cdot (HmtpO) \cdot H_2O$ [34], both coordinated and non-coordinated triazolopyrimidine molecules coexist in the compound, interacting via stacking or hydrogen bonding. These were the only references to the uncoordinated neutral ligands till the structure of HmtpO itself was solved [28].

The protonated form of dmtp has been found as the counterion of complex anions such as $[CdBr_4]^{2-}$ [35] and $[SnCl_6]^{2-}$ [36]. The protonation of dmtp takes place at N3, which results in an opening of the C2–N3–C3a angle. In the latter, cations associate in hydrogen bonded N3–H...N4 couples, analogous to those present in Ag(I) and Cu(I) compounds (see below). On the other hand, a compound has also been described in which the anionic form of HmtpO balances the charge of the $[Cu(H_2O)_2(\textit{cis}\text{-}1,2\text{-diaminocyclohexane})_2]^{2+}$ cation [37].

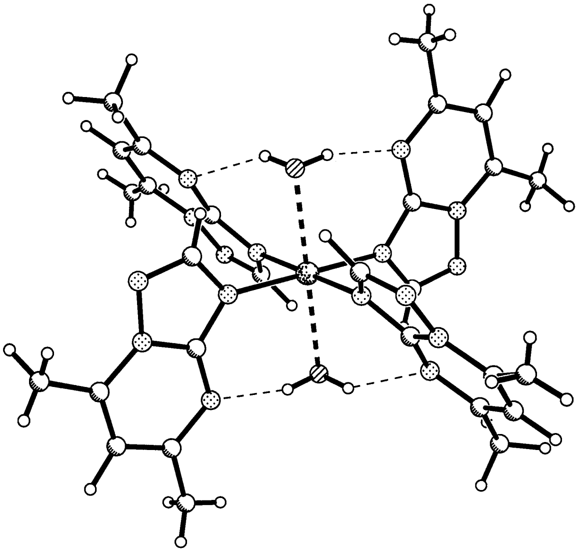


Fig. 4. View of the $[Cu(dmtp)_4(H_2O)_2]^{2+}$ cation. Adapted from Favre et al. [40].

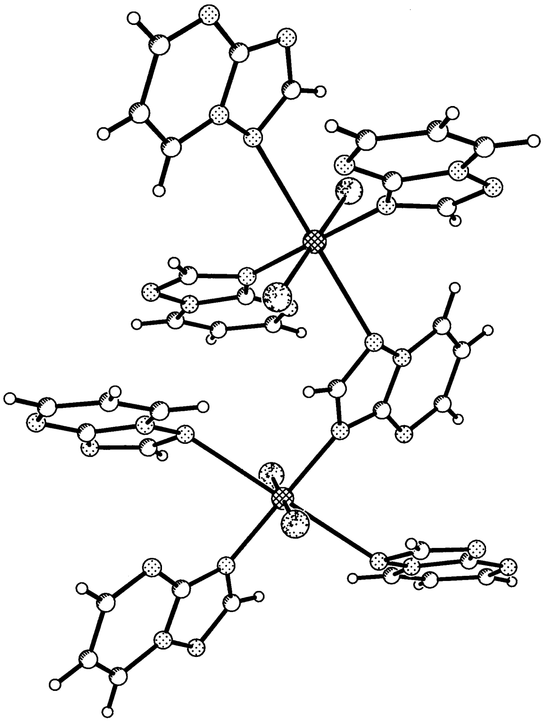


Fig. 5. Polymeric structure of [$CuCl_2(tp)_2$] Adapted from Biagini-Cingi et al. [43].

4. Copper(II) complexes

As it happens with other ligands, copper(II) is the metal ion of which more complexes have been characterized. Most of them exhibit the geometries expected from the Jahn–Teller theorem: either elongated octahedrons or square pyramids, with four ligands strongly coordinated in a square-planar arrangement and one or two interacting more weakly in apical positions. The only exceptions to this are [$Cu(NCS)_2(6mtp)_2$] [10], a very distorted tetrahedron, [$CuBr_2(tp)_2(H_2O)$] [38] and [$Cu_2Br_4(dmtp)_2$]·$2H_2O$ [39], trigonal bipyramids. Selected geometrical parameters for copper complexes are collected in Table 1.

The main binding site is N3, which usually occupies a equatorial position strongly bonded to the metal atom at around 2.0 Å, the only exception to this being one of the mtpO$^-$ ligands in [$Cu(mtpO)_2(tn)$]·$2H_2O$ [24] that binds bidentately through N1 and O7 (Fig. 3) and the mtpO$^-$ ligands in [$Cu(mtpO)_2(en)_2$] [37] with N3 occupying axial positions.

Many of these compounds are mononuclear, namely [$Cu(NCS)_2(6mtp)_2$] [10], [$CuBr_2(tp)_2(H_2O)$] [38], [$Cu(dmtp)_4(H_2O)_2$]$(PF_6)_2$ [40], [$Cu(mtpO)_2(NH_3)_2$·$(H_2O)_2$] [41], [$Cu(mtpO)_2(H_2O)_4$] [41], [$Cu(dmtp)_3(H_2O)_2$]$(ClO_4)_2$·$2H_2O$ [42], [$Cu(mtpO)_2(en)_2$] [37], [$Cu(mtpO)_2(en)(H_2O)$]·H_2O [24], [$Cu(NO_3)_2(HmtpO)_2$-

$(H_2O)_2] \cdot 2H_2O$ [24], $[Cu(mtpO)_2(tn)] \cdot 2H_2O$ [24], $[Cu(mtpO)_2(py)_2(H_2O)_2]$ [24], $[Cu(mtpO)_2(bpy)(H_2O)] \cdot EtOH \cdot H_2O$ [24] and $[Cu(mtpO)_2(phen)(H_2O)_2]$ [24]. An example of this type of compounds is displayed in Fig. 4.

In some cases, the organic derivative not only binds via N3 but also via N1, which occupies one axial position of a second copper atom, two-dimensional polymers being generated in this way (see Fig. 5). This is the case for $[Cu(NCS)_2(5mtp)_2]$ [10], $[CuCl_2(tp)_2]$ [43] and $[Cu(NCS)_2(tp)_2]$ [43]; two forms have been isolated for the latter but only one of them has been crystallographically characterized.

On the other hand, bidentate N3–N4 behaviour, common for Ag(I), Pd(II) and Pt(II) (see below) has been observed for the first time for Cu(II) in the dimeric compound $[Cu_2(5tpO)_4(H_2O)_2] \cdot 2H_2O$ [44], in which a strong antiferromagnetic coupling ($2J = -104.9$ cm^{-1}) takes place through the triazolopyrimidine moieties.

Dimeric compounds have also been characterized in which the auxiliary anions bridge the metallic atoms. This is observed for $[Cu_2Br_4(dmtp)_2] \cdot 2H_2O$ [39], in which the copper atoms are antiferromagnetically coupled with $2J = -21.1$ cm^{-1}: in this work, the value of $2J$ is correlated with the structure for a number of bromine bridged copper dimers. Two isomers with the formula $[Cu_2(NCS)_4(dmtp)_4]$ have been structurally characterized (they are shown in Fig. 6), the bridging thiocyanate group being *N*-equatorial *S*-axial [45] in one of them and *S*-equatorial *N*-axial in the other [46], whereas both atoms are equatorial in the compound $[Cu_2(NCS)_4(HmtpO)_2(H_2O)_2]$ [9]: as a consequence of this disposition a very strong antiferromagnetic coupling ($2J = -148.2$ cm^{-1}) is observed in the latter whereas a very weak magnetic interaction is observed in the two isomers containing the ligand dmtp.

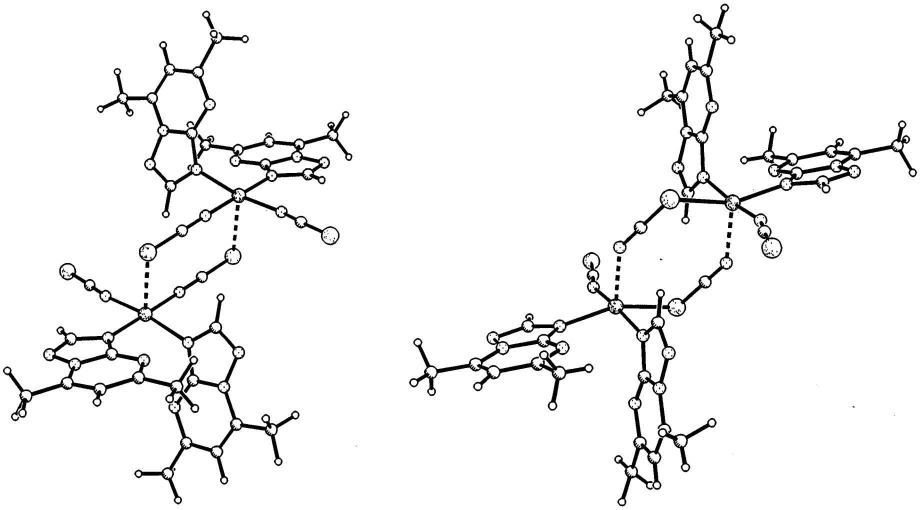


Fig. 6. α (axial bridging–S, left) and β (axial bridging–N, right) isomers of $[Cu_2(NCS)_4(dmtp)_4]$. Adapted from Biagini-Cingi et al. [45] and Haasnoot et al. [46].

Table 2
Bond distances in divalent metal (excepted Cu, Pd, Pt) complexes

Compound	Geometry	Distance/Å	Reference
$[Mn(Htpo_2)_2(H_2O)_2]$	Oct.	2.251(1) (Mn–N1)	[11]
		2.193(1) (Mn–O7)	
$[Fe(NCS)_2(5mtp)_2(H_2O)_2]$	Oct.	2.225(5) (Fe–N3)	[47]
$[Fe(NCS)_2(tp)_2]$	Oct.	2.23(2) (Fe–N1)	[54]
		2.25(2) (Fe–N3)	
$[Co(NCS)_2(5mtp)_2(H_2O)_2]$	Oct.	2.173(3) (Co–N3)	[48]
$[Co(dmtp)_2(H_2O)_4](NO_3)_2$	Oct.	2.170(6) (Co–N3)	[49]
$[Co(dmtp)_2(H_2O)_4]Br_2 \cdot 2H_2O$	Oct.	2.116(6) (Co–N3)	[50]
$[CoCl_2(dptp)_2]$	Tetr.	2.020(3) (Co–N3)	[56]
$[Ni(dmtp)_2(H_2O)_4]I_2 \cdot 2H_2O$	Oct.	2.086(6) (Ni–N3)	[33]
$[Ni(dmtp)_4(H_2O)_2](I_3)_2 \cdot (dmtp)_2$	Oct.	2.07(2) (Ni–N3)	[33]
		2.09(2) (Ni–N3)	
$[Ni(NCS)_2(5HtpO)_2(H_2O)_2]$	Oct.	2.132(4) (Ni–N3)	[51]
$[ZnCl_2(dptp)_2]$	Tetr.	2.022(2) (Zn–N3)	[56]
$[ZnBr_2(tp)_2] \cdot \frac{1}{2}H_2O$	Tetr.	2.023(4) (Zn–N3)	[58]
		2.034(4) (Zn–N3)	
		2.038(4) (Zn–N3)	
		2.041(4) (Zn–N3)	
$[ZnCl_2(dmtp)_2]$	Tetr.	2.058(2) (Zn–N3)	[57]
		2.020(2) (Zn–N3)	
$[ZnBr_2(dmtp)_2]$	Tetr.	2.064(5) (Zn–N3)	[35]
		2.015(4) (Zn–N3)	
$[Zn(mtpO)_2(en)_2]$	Oct.	2.319(1) (Zn–N3)	[52]
$[Zn(mtpO)_2(py)_2(H_2O)_2]$	Oct.	2.164(3) (Zn–N3)	[52]
$[Cd(dmtp)_2(H_2O)_4](NO_3)_2$	Oct.	2.317(3) (Cd–N3)	[49]
$[Cd(SO_4)(dmtp)(H_2O)_2]$	Oct.	2.359(3) (Cd–N3)	[55]
$[Cd(NCS)_2(dmtp)_2(H_2O)_2]$	Oct.	2.366(2) (Cd–N3)	[53]
$[HgCl_2(dmtp)_2]$	Tetr.	2.290(6) (Hg–N3)	[35]
		2.395(5) (Hg–N3)	
$[Hg(SCN)_2(dmtp)_2]$	Tetr.	2.38(1) (Hg–N3)	[53]
		2.418(8) (Hg–N3)	
$[HgCl_2(HmtpO)]_2 \cdot HmtpO \cdot H_2O$	Trig.	2.63(1) (Hg–N1)	[34]
		2.46(2) (Hg–N1)	

Finally, a number of dmtp-Cu(II) compounds with diverse stoichiometry have been spectroscopically but not crystallographically characterized [40], N3 monodentate coordination being proposed for them.

5. Manganese, iron, cobalt, nickel, zinc, cadmium and mercury complexes

A number of Mn(II), Fe(II), Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) complexes with triazolo-[1,5-a]pyrimidine derivatives have been prepared and the crystal structures of some of them have been determined by single crystal X-ray diffraction (see Table 2). The complexes have been synthesized in a similar way from an aqueous solution of the corresponding ligand and different metal salts in a 2:1 ratio by slow evaporation of the solvent. In a few cases ethanol or acetone was used as solvent.

The most frequent geometry found in the structural analysis is octahedral with two (or four) triazolo-[1,5-a]pyrimidine ligands monodentately coordinated via the nitrogen atom in position 3. The coordination sphere is completed by water molecules, auxiliary amine ligands or NCS^- anions, other anions balancing the charge of cationic complexes. The following compounds obey this scheme: $[Fe(NCS)_2(5mtp)_2(H_2O)_2]$ [47], $[Co(NCS)_2(5mtp)_2(H_2O)_2]$ [48], $[Co(dmtp)_2(H_2O)_4](NO_3)_2$ [49], $[Co(dmtp)_2(H_2O)_4]Br_2 \cdot 2H_2O$ [50], $[Ni(dmtp)_2(H_2O)_4]I_2 \cdot 2H_2O$ [33], $[Ni(dmtp)_4(H_2O)_2](I_3)_2 \cdot (dmtp)_2$ [33], $[Ni(NCS)_2(5HtpO)_2(H_2O)_2]$ [51], $[Zn(mtpO)_2(en)_2]$ [52], $[Zn(mtpO)_2(py)_2(H_2O)_2]$ [52], $[Cd(dmtp)_2(H_2O)_4](NO_3)_2$ [49] and $[Cd(NCS)_2(dmtp)_2(H_2O)_2]$ [53]. All-*trans* configurations are present in all cases except for those with formulae $[M(NCS)_2L_2(H_2O)_2]$ ($L = 5mtp$, dmtp), with primary ligands in trans and NCS^- and H_2O in *cis* (Fig. 7). The primary ligands are neutral except in $[Zn(mtpO)_2(en)_2]$ and $[Zn(mtpO)_2(py)_2(H_2O)_2]$, with the anionic form of HmtpO.

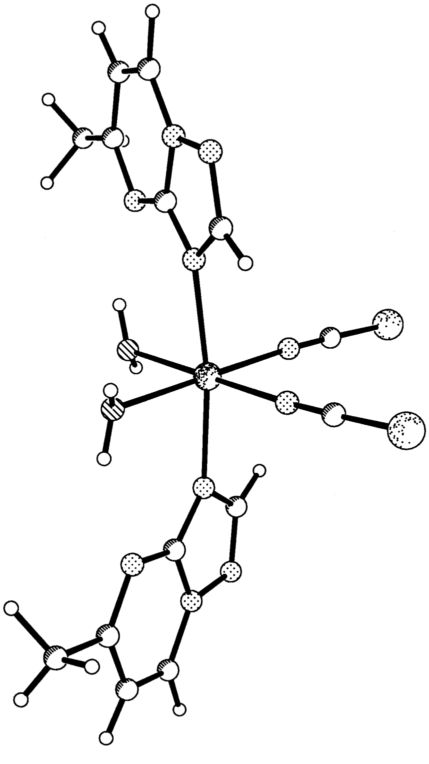


Fig. 7. Molecular structure of $[Fe(NCS)_2(5mtp)_2(H_2O)_2]$. Adapted from Biagini-Cingi et al. [47].

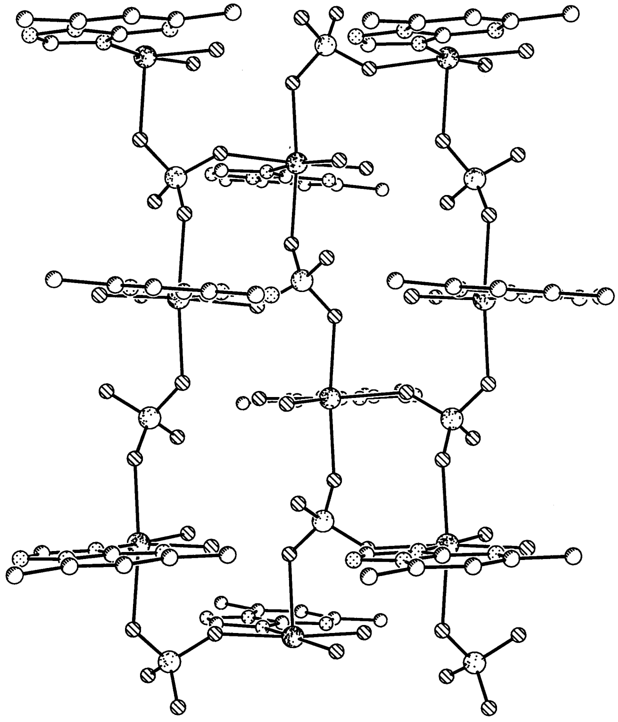


Fig. 8. Bidimensional polymeric structure of $[Cd(SO_4)(dmtp)(H_2O)_2]$. Adapted from Rahmani et al. [55].

$[Mn(HtpO_2)_2(H_2O)_2]$ [11] is also monomeric and octahedral but the ligand is coordinated bidentately through N1 and O7 instead of N3-monodentately as the previous ones, which is justified by the electronic nature of the anion $HtpO_2^-$. On the other hand, distorted octahedral geometry is present in the compounds $[Fe(NCS)_2(tp)_2]$ [54] and $[Cd(SO_4)(dmtp)(H_2O)_2]$ [55], these compounds not being monomeric but bidimensionally polymeric; in the former, each ligand bridges two iron atoms via N1 and N3 and the distance Fe–NCS is quite short (2.056(8) Å) whereas in the later dmtp is N3-monodentate and the polymer is built by the presence of triple bridging (μ_3–SO_4^{2-}) sulphate anions: in this compound, every cadmium atom is linked to oxygen atoms from three different sulphato groups, two water oxygen atoms and N3 from dmtp (see Fig. 8).

There is a number of complexes with distorted tetrahedral geometry, with general formula $[ML_2X_2]$; they are $[CoCl_2(dptp)_2]$ [56], $[ZnCl_2(dptp)_2]$ [56], $[ZnCl_2(dmtp)_2]$ [57], $[ZnBr_2(dmtp)_2]$ [35] $[ZnBr_2(tp)_2]\cdot\frac{1}{2}H_2O$ [58], $[HgCl_2(dmtp)_2]$ [35] and $[Hg(SCN)_2(dmtp)_2]$ [53]. All of them are monomeric with organic ligands monodentately coordinated via N3.

A special case is $[HgCl_2(HmtpO)]_2\cdot(HmtpO)\cdot H_2O$ [34], the structure of which is built by two crystallographically different $HgCl_2(Hmtpo)$ entities, solvation water and uncoordinated HmtpO molecules. Metal atoms are located in a distorted trigonal geometry comprising two chlorine atoms and a nitrogen atom N1 from a monodentate HmtpO moiety, this coordination mode being unique for this ligand. Mercury atoms also interact weakly with chlorine atoms from neighbouring $HgCl_2HmtpO$ units, a single and a double chain growing along the crystallographic a axis being generated for the two crystallographically independent Hg atoms (Fig. 9).

Finally, the synthesis and characterization by means of spectroscopy, X-ray powder diagrams and magnetic methods of around forty compounds have been performed without a single crystal X-ray determination [11,33–35,50,53–55,59,60]. Structures are proposed on the basis of the results obtained and comparison with other compounds for which the crystallographic structure is available.

6. Heterometallic compounds including Hg(II)

The crystal structure of a few heterometallic mercury(II) complexes with the ligand dmtp have been described; these complexes are: $[FeHg(NCS)_4(dmtp)_2(H_2O)_{1.5}]$ [61], $[FeHg(NCS)_4(dmtp)_2(H_2O)]$ [61], $[FeHg(NCS)_4(dmtp)(H_2O)](Me_2CO)$ [61], $[CoHg(NCS)_4(dmtp)_3(H_2O)]_2$ [62] and $[CuHg(NCS)_3(dmtp)_2]$ [63]. The manganese and nickel complexes analogous to the cobalt compound have been characterized spectroscopically and by powder X-ray diagrams [62].

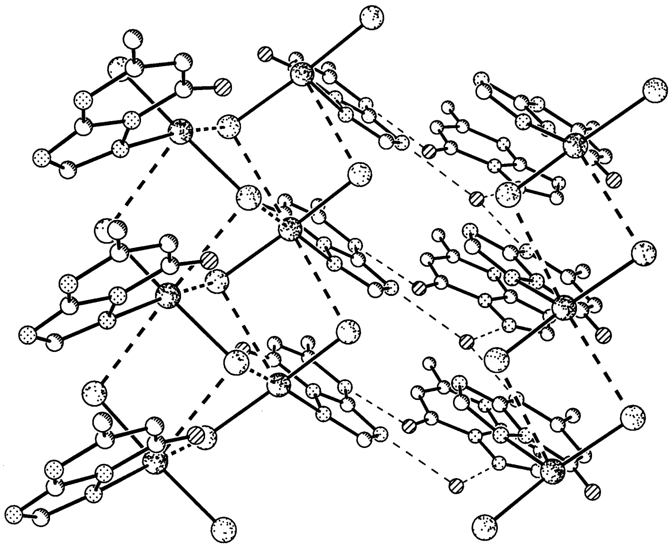


Fig. 9. Double (left) and single (right) chains present in the crystal structure of $[HgCl_2(HmtpO)]_2 \cdot HmtpO \cdot H_2O$. Both chains are linked via hydrogen bonds with the non coordinated HmtpO molecule and the water molecule. Adapted from Salas et al. [34].

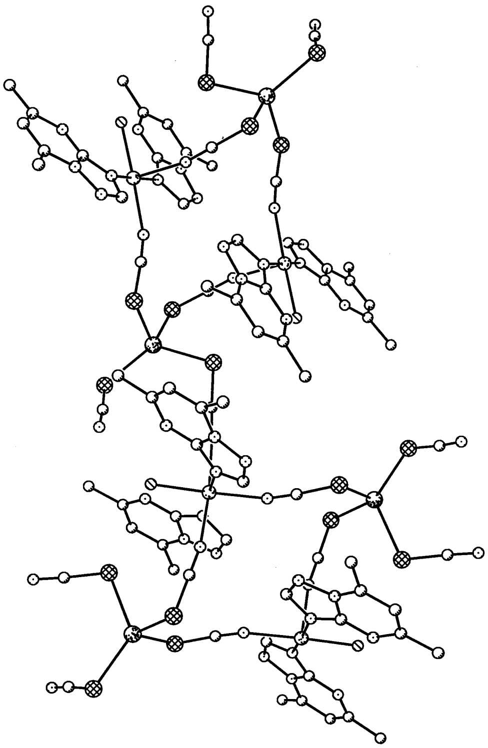


Fig. 10. Bidimensional polymeric structure of [FeHg$(SCN)_4$$(dmtp)_2$$(H_2O)$]. Adapted from Biagini-Cingi et al. [61].

In all cases, Hg–SCN–M bridges are present which generate either dimeric (cobalt compound) or polymeric structures (the rest, see for example Fig. 10) and the dmtp ligands coordinate monodentately via N3. In both iron and cobalt complexes the mercury atom is tetrahedrally coordinated by sulphur atoms from thiocyanate groups and the dmtp molecules are coordinated only to Co(II) and Fe(II) in an octahedral environment. In the crystal structure of [CuHg$(NCS)_3$$(dmtp)_2$], both Hg(II) and Cu(I) metals are in a tetrahedral environment with three thiocyanate groups (via S for Hg and via N for Cu) and a dmtp molecule. Table 3 collects the M–N3 distances for all these compounds.

7. Silver(I) and copper(I) complexes

A number of silver(I) complexes with triazolo-[1,5-a]pyrimidine derivatives have been described, starting with the 1:1 compound with the anion mtpO$^-$ [64], this study having been performed in relation with the use of HmtpO for stabilizing photographic emulsions.

The basic structural unit in most of these silver complexes is an eight-member ring –Ag–N–C–N–Ag–N–C–N– generated by the coordination of two triazolopyrimidine moieties to two silver atoms through the nitrogen atoms in positions 3 and 4 (see Fig. 11). A relatively short Ag–Ag contact (3.0–3.2 Å, see Table 4) is generated in this way and the possible direct interaction between the metal centres has been examined by means of ab initio MO calculations [65], suggesting the existence of a significant Ag–Ag interaction. The coordination sphere is then formed by two strongly coordinated nitrogen atoms of the organic derivative in a approximately linear fashion and a variable number of other more weakly attached atoms from the counteranions or from water molecules.

Such dimeric basic units associate in a number of different ways to build the crystal structures: they can be relatively isolated as it happens in $[Ag_2(HSO_4)_2(dmtp)_2]\cdot 4H_2O$ [66] and $[Ag_2(NO_3)_2(tp)_2]$ [67] or bridged by the anions as in $[Ag_2(NO_3)_2(dmtp)_2]$ [65] and $[Ag_2(SO_4)(tp)_2(H_2O)]\cdot H_2O$ [67]. In the case of $[Ag_2(mtpO)_2]$ [64], the dimeric units are linked by weak bonds of silver atoms with the N1 and O7 atoms of neighbouring units, whereas a third silver atom is present in $[Ag_3(HSO_4)(mtpO)_2(H_2O)_2]\cdot H_2O$ [28], coordinated to the N1 and O7 atoms of two different dimeric units, generating a linear polymer in this way (Fig. 12); extra Ag–Ag interactions (at 3.268(1) Å), unsupported by bridging ligands are present in this compound.

A curious structure is that of $[Ag_2(SO_4)(dmtp)_2][Ag_2(HSO_4)_2(dmtp)_2]\cdot H_2O$ [66]: two different dimers coexist in the same crystal: the first is centrosymmetric (both silver atoms coordinated by a N3 atom from one organic ligand and a N4 atom

Table 3
Bond distances in heterometallic Hg–M complexes

Compound	Metal and attached atoms[a]	M–N3/Å	Reference
$[FeHg(SCN)_4(dmtp)_2(H_2O)_{1.5}]$	Fe: N3,N3,Nt,Nt,Nt,Ow	2.211(14) 2.215(13)	[61]
	Fe: N3,N3,Nt,Nt,Ow,Ow	2.186(1) 2.208(12)	
	Hg: St,St,St,St	–	
$[FeHg(SCN)_4(dmtp)_2(H_2O)]$	Fe: N3,N3,Nt,Nt,Nt,Ow	2.169(12) 2.165(11)	[61]
	Hg: St,St,St,St	–	
$[FeHg(SCN)_4(dmtp)(H_2O)_2]\cdot(Me_2CO)$	Fe: N3,Nt,Nt,Nt,Ow,Ow	2.246(17)	[61]
	Hg: St,St,St,St	–	
$[CoHg(SCN)_4(dmtp)_3(H_2O)]_2$	Co: N3,N3,N3,Nt,Nt,Ow	2.140(10) 2.177(10) 2.108(9)	[62]
	Hg:St,St,St,St	–	
$[CuHg(SCN)_3(dmtp)_2]$	Cu: N3,Nt,Nt,Nt	2.06(2) 2.00(2)	[63]
	Hg: N3,St,St,St	2.372(19) 2.557(5)	

[a] Nt,St = N and S atoms of thiocyanate group. Ow = O atom of water.

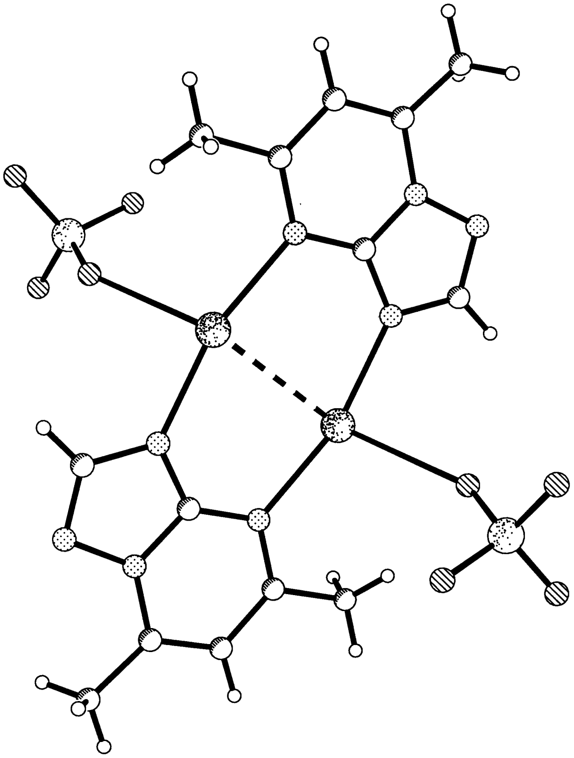


Fig. 11. Molecular structure of the dimer [$Ag_2(HSO_4)_2(dmtp)_2$]. Adapted from Salas et al. [66].

from the other) and the second has C_2 symmetry (one silver atom coordinated by two N3 atoms and the other coordinated by two N4 atoms). Centrosymmetric dimers are bridged by the sulphato groups to build a zig-zag chain with the C_2 dimers occupying the gaps in the chain. On the other hand, three rather than two N3–N4 coordinated bridging ligands join the two metal atoms in [$Ag_2(SO_4)(tp)_3(H_2O)$] · $3H_2O$ [67].

Two compounds have been also described in which the above mentioned dimeric units are not present: [$Ag(NO_3)(HmtpO)$]$_n$ and [$Ag(ClO_4)(HmtpO)(PPh_3)$]$_n$ [28]. The structure of these compounds is a linear polymer with the metal atoms coordinated by N1 and N3 from two different HmtpO molecules (O7 also cooperates with N1 in the first case). The presence of the phosphine ligand considerably weakens the Ag–N1 bond (2.253(8) Å in the first compound and 2.597(2) Å in the second).

Finally, there is only one copper(I) compound, the structure of which has been solved, [$Cu_4Cl_2(dmtp)_4$][Cu_2Cl_4] [68]. It is built by two dimeric units, analogous to the silver(I) previously described with a Cu–Cu distance of 2.909 Å, linked by two bridging chlorine atoms (Fig. 13).

Table 4
Distances within the –Ag–N–C–N–Ag–N–C–N– cores

Compound	Ag–Ag/Å	Ag–N3/Å	Ag–N4/Å	Reference
$[Ag_2(HSO_4)_2(dmtp)_2]\cdot 4H_2O$	2.988(1)	2.164(4)	2.187(3)	[66]
$[Ag_2(NO_3)_2(tp)_2]$	3.117(1)	2.165(2)	2.220(2)	[67]
$[Ag_2(NO_3)_2(dmtp)_2]$	3.058(1)	2.210(2)	2.250(2)	[65]
$[Ag_2(SO_4)(tp)_2(H_2O)]\cdot H_2O$	3.1266(6)	2.140(6)	2.261(6)	[67]
		2.142(6)	2.242(6)	
$[Ag_2(mtpO)_2]$	3.187	2.168	2.188	[64]
$[Ag_3(mtpO)_2(HSO_4)(H_2O)_2]\cdot H_2O$	3.078(1)	2.176(5)	2.159(5)	[28]
		2.154(5)	2.186(6)	
$[Ag_2(SO_4)(dmtp)_2][Ag_2(HSO_4)_2(dmtp)_2]\cdot H_2O$, dimer A	3.100(2)	2.177(9)	2.220(9)	[66]
$[Ag_2(SO_4)(dmtp)_2][Ag_2(HSO_4)_2(dmtp)_2]\cdot H_2O$, dimer B	3.013(2)	2.115(9)	2.366(9)	[66]
$[Ag_2(SO_4)(tp)_3(H_2O)]\cdot 3H_2O$	3.089(1)	2.188(8)	2.351(6)	[67]
		2.271(7)	2.274(8)	

8. Platinum group metal complexes

The study of the interaction of platinum group metals with 1,2,4–triazolo-[1,5-a]pyrimidine ligands is dominated by the formation of Pt(II) and Pd(II) complexes, with only one example for a Ru(III) compound.

For the ligand dmtp, that has not any ionizable hydrogen atom, the structures of only three mononuclear complexes have been reported: *mer*-$[RuCl_3(dmtp)_2(H_2O)]$ [69], *trans*-$[PdBr_2(dmtp)_2]\cdot CH_3OH$ [70] and $[Pt(dmtp)_4][Pt(SCN)_6]$ [45]. In each case, the triazolopyrimidine ligand binds only via N3, the Ru–N bond (2.092(4) Å) being significantly longer than the Pd–N and Pt–N (2.00 ± 0.03 Å). In *trans*-$[PdBr_2(dmtp)_2]$, the ligands are disposed in a head to tail orientation, whereas in $[RuCl_3(dmtp)_2(H_2O)]$, the head to head atropoisomer is present (Fig. 14), stabilized by a water molecule hydrogen bonded to N4 atoms of both organic ligands.

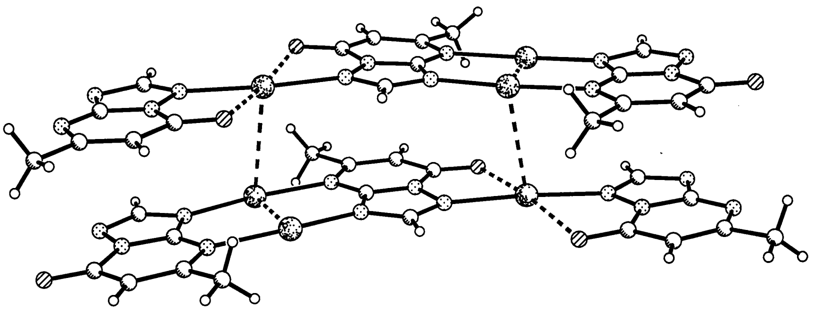


Fig. 12. Polymeric chains in $[Ag_3(mtpO)_2(HSO_4)(H_2O)_2]\cdot H_2O$. Bisulphate anions and water molecules are omitted for clarity. Adapted from Navarro et al. [28].

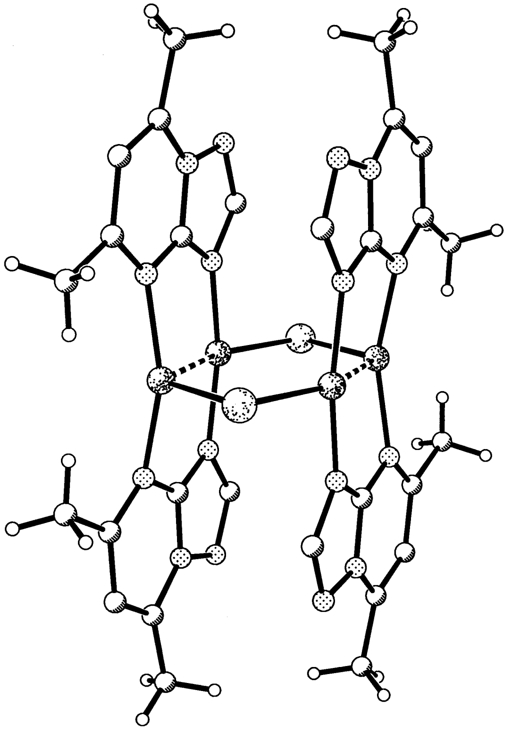


Fig. 13. View of the $[Cu_4Cl_2(dmtp)_4]^{2+}$ cation. Adapted from Haasnoot et al. [68].

On the other hand, because of the presence of an ionizable hydrogen at N4, HmtpO is a well suited ligand for the preparation of multinuclear metal complexes, since it provides up to four potential binding sites, N3 and N4 being adequate to coordinate soft atoms such as Pt(II) and Pd(II). In a first stage in acidic media, the mononuclear species monodentately coordinated via N3 are formed, *cis*-$[PtCl_2(HmtpO)_2] \cdot 2H_2O$ [71] and *cis*-$[Pt(NH_3)_2(HmtpO)_2](NO_3)_2 \cdot 2H_2O$ [72] having been characterized crystallographically. In the former, the head to head atropoisomer is present (stabilized by hydrogen bonds as in the above mentioned Ru compound) whereas the disposition is head to tail in the latter. The reactivity of *cis*-$[PtCl_2(HmtpO)_2]$ towards the model nucleobase 9-ethylguanine (9-EtGH) has been investigated by ^{1}H-NMR spectroscopy at 45°C in aqueous media, the product *cis*-$[Pt(mtpO\text{-}N^3)_2\ (9EtGH{-}N^7)_2]$ having been detected [71].

If the pH is raised up to 7, deprotonation of HmtpO at N4 occurs and the monomeric compound *cis*-$[PtCl_2(HmtpO)_2]$ condensate with itself yielding the dinuclear product $[Pt_2(mtpO)_4]$, the structure of the DMSO solvate of this compound having been determined [73] (Fig. 15): in this compound, the two Pt atoms are bridged by four mtpO ligands, with a quite short Pt–Pt distance (2.744(2) Å). The Pt–Pt interaction is reflected in the ^{195}Pt-NMR spectrum by the great deshielding observed for the metal nuclei ($\delta = -2005$ ppm). Despite this, the compound is

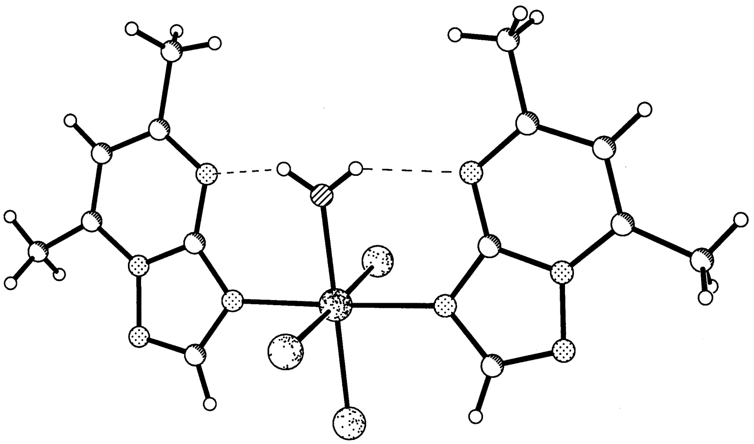


Fig. 14. Molecular structure of *mer*-[$RuCl_3(dmtp)_2(H_2O)$]. Adapted from Velders et al. [69].

inert toward oxidation. The Pt–Pt interaction has been also studied theoretically in the analogous model compound $Pt_2[NHCHN(C(CH_2)(CH_3))]_4$ [73].

The reaction of *cis*-[$Pt(NH_3)_2(HmtpO)_2](NO_3)_2 \cdot 2H_2O$ with palladium electrophiles of the type $[Pd(H_2O)_2(L–L)]^{2+}$ (where L–L is a bidentate diamine)

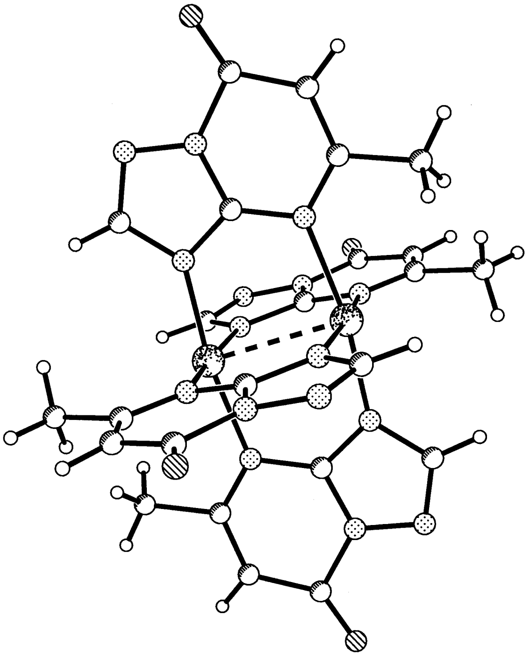


Fig. 15. Molecular structure of the dimer [$Pt_2(mtpO)_4$]. Adapted from Navarro et al. [73].

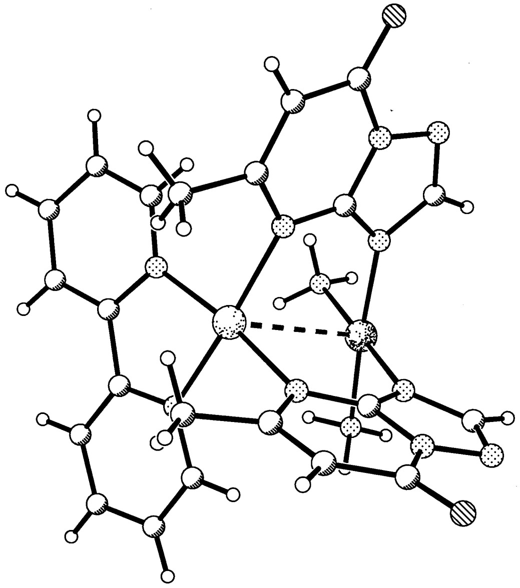


Fig. 16. View of the dinuclear cation $[(NH_3)_2Pt(mtpO)_2Pd(bpy)]^{2+}$. Adapted from Navarro et al. [72].

affords heterobinuclear complexes of formula $[(NH_3)_2Pt(mtpO)_2Pd(L-L)](NO_3)_2$ [72]. The compounds have been characterized by bidimensional ^1H spectroscopy and the structure of that with L–L = bipyridine has been solved (Fig. 16). The ligands coordinate via N3 to Pt and via N4 to Pd and the Pt–Pd separation is 3.083(1) Å.

On the other hand, the reaction of *cis*-$[Pt(NH_3)_2(HmtpO)_2]^{2+}$ with Pt electrophiles is different to those of Pd [72]. Thus, with $[Pt(H_2O)_2(bpy)]^{2+}$, the reaction appears to stop before completion yielding the compound $[(mtpO-N^3)(NH_3)_2Pt(\mu-mtpO-N^3,N^4)Pt(bpy)(OH)](NO_3)\cdot 6H_2O$, and with *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ it is shown by ^1H-NMR spectroscopy that the second platinum centre clearly does not bind to N4 but possibly to N1, which may lead to the formation of polymeric or cyclic species.

Binuclear Pd–Pd compounds have also been obtained, in this case by the reaction of the $[Pd(H_2O)_2(L-L)](NO_3)_2$ electrophiles with HmtpO in 1:1 molar ratio in aqueous media at pH 7–8. The compounds obtained display general formula $[Pd_2(\mu-mtpO-N^3,N^4)_2(L-L)_2](NO_3)_2$ [74]. The compounds have been characterized by one and two-dimensional ^1H- and ^{13}C-NMR spectroscopy and single crystal X-ray diffraction (ethylendiammine and bipyridine complexes). The two $mtpO^-$ ligands are arranged in a head to tail orientation and the Pd–Pd separation appears to be modulated by the interactions between the auxiliary ligands L–L (3.225(1) and 3.034(1) Å, respectively).

9. Biological activity

A number of the isolated metal complexes of triazolo-[1,5-a]pyrimidine have been tested to know their possible biological activity. In this way, several divalent metal complexes of dmtp have been tested as inhibitors of the growth of different Gram(+) and Gram(−) bacteria and the fungus *Candida albicans*. Some cobalt(II) complexes show an appreciable activity against *Micrococcus*, *Staphylococcus* and *Proteus* [50] and some copper(II) compounds present MIC (minimum inhibitory concentration) values lower than 50 μg cm^{-3} towards the Gram(−) bacteria *E. coli* and *Salmonella* Sp. [39]. Likewise, MIC values of 20 μg cm^{-3} have been found for $[Ni(dmtp)(SO_4)(H_2O)] \cdot 4H_2O$ against *Streptococcus faecalis* [55] and $[Cd(dmtp)X_2(H_2O)]$ (where X = Cl,Br) against *Staphilococcus aureus*, *Streptococcus faecalis* and *Bacillus megaterium* [35].

The effect of several metal complexes of HmtpO against *Phytomonas staheli* (promastigote form) has also been studied [75,76] showing that some of them inhibit parasite growth by nearly 90%; these complexes have also displayed good results against analogous parasites like *Trypanosoma cruzi* and *Leishmania donovani*. Transmission electron microscopy studies have been carried out to evaluate the morphological changes that these complexes cause in the different cell organelles, comparing the cell structure of treated and nontreated *P. staheli* [77].

The effect of *cis*-$[PtCl_2(HmtpO)_2]$ addition at different concentrations to cultured human cell lines MCF-7 breast carcinoma and A121 ovarian carcinoma has been tested [71]. The results indicate a high antitumour activity against the latter, this complex being less active than cisplatin but more than carboplatin. Some dmtp complexes with Ru(III) are also being tested for antitumour activity [69].

10. Conclusions

This review shows the versatility of 1,2,4-triazolo-[1,5-a]pyrimidine ligands to bind metal ions through different positions. However, the main binding site is, in the vast majority of cases, the nitrogen atom in position 3, which uses to be (almost always) the only binding site when the ligands are monodentate.

The cooperation of N1 with N3 usually gives rise to the formation of polymeric compounds whereas dimers with eight-member –M–N–C–N–M–N–C–N– rings are formed when the bridging mode is N3,N4 bidentate (M = Ag(I), Cu(I), Cu(II), Pt(II), Pd(II) or even H^+). This latter coordination mode provokes short intermetallic contacts with the possibility of metal–metal direct interactions that may be studied either experimentally by magnetic susceptibility or NMR measurements or theoretically by MO calculations.

The presence of exocyclic oxygen atoms at positions 5 and/or 7 introduces the possibility of deprotonation, usually favouring the involvement of N4 in binding. An oxygen atom in position 7 adds another possible binding mode, a N1–O7 chelate that has been observed in a few cases.

The presence of the triazolopyrimidine ligand also influences in some cases the behaviour of other present ligands, nuclear and polynuclear compounds bridged by these auxiliary ligands having also been described with metal atoms interacting through them.

The similarity of these ligands with biologically important molecules makes their complexes suitable for possible biological activity. Several compounds have been tested for antimicrobial and antitumoural activity, positive results having been obtained for a few of them.

Appendix A. Abbreviations

tp	1,2,4-triazolo-[1,5-a]pyrimidine
5mtp	5-methyl-1,2,4-triazolo-[1,5-a]pyrimidine
6mtp	6-methyl-1,2,4-triazolo-[1,5-a]pyrimidine
dmtp	5,7-dimethyl-1,2,4-triazolo-[1,5-a]pyrimidine
dptp	5,7-diphenyl-1,2,4-triazolo-[1,5-a]pyrimidine
5HtpO	4,5-dihydro-5-oxo-1,2,4-triazolo-[1,5-a]pyrimidine
7HtpO	4,7-dihydro-7-oxo-1,2,4-triazolo-[1,5-a]pyrimidine
HmtpO	4,7-dihydro-5-methyl-7-oxo-1,2,4-triazolo-[1,5-a]pyrimidine
H_2tpO_2	4,5,6,7-tetrahydro-5,7-dioxo-1,2,4-triazolo-[1,5-a]pyrimidine
en	ethylendiamine
tn	1,3-diaminopropane
py	pyridine
bpy	2,2′-bipyridine
phen	phenantroline
PPh_3	triphenylphospine

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