1,2,4,5-Tetrazine: an unprecedented μ_4-coordination that enhances ability for anion···π interactions†

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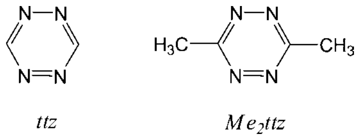
A series of framework coordination polymers reveals the use of 1,2,4,5-tetrazines as efficient bridging ligands towards silver(I) and copper(I) ions. All four nitrogen atoms were functional as lone pair donors leading to an unprecedented μ_4-coordination of the ligands (1,2,4,5-tetrazine, ttz; 3,6-dimethyl-1,2,4,5-tetrazine, Me_2ttz) in $[Ag(ttz)(X)]$ ($X = NO_3$, **1**; ClO_4, **2**), $[Ag_2(Me_2ttz)(NO_3)_2]$ (**3**), $[Ag_2(Me_2ttz)(H_2O)_2(ClO_4)_2]$ (**4**), $[Ag_3(Me_2ttz)(H_2O)_2(CF_3SO_3)_3]$ (**5**) and $[Cu_4Cl_4(Me_2ttz)]$ (**6**). In **1** and **2**, μ_4-tetrazines and silver ions (AgN_4, Ag–N 2.42–2.53 Å) compose a 3D framework of $\{4^2;8^4\}$ topology. Structures **3** and **4** were based on disilver–tetrazine ribbons, while in **5** μ_4-tetrazines interconnect silver–triflate chains. In **6**, μ_4-ligands connect inorganic layers sustained by copper–chloride squares, hexa- and octagons (1.974(2) and 1.981(2) Å). Multiple N-coordination to metal ions enhances the ability of the electron deficient tetrazine system for anion···π binding. Compounds **1** and **2** exhibit very short interactions of this type with corresponding O···C(N) separations down to a record value of 2.78 Å and O···π 2.61 Å. For **6**, π-acidity of tetrazine was reflected by contacts Cl···π of 3.30 Å. Results of high level *ab initio* calculations (RI-MP2/aug-cc-pVTZ) were in good agreement with experimental results, and were suggestive of the progressive enhancement of the π-acidity by increasing the number of Ag(I) ions N-coordinated to tetrazine.

Introduction

Non-covalent interactions are of paramount importance in many areas of modern chemistry. They are important in controlling the conformation of the molecules[1] in chemical reactions, in molecular recognition and in regulating biochemical processes.[2] These processes are achieved with specific, efficient and intricate combinations of weak intermolecular forces. Non-covalent interactions such as hydrogen bonding, anion···π, cation···π and π···π interactions, and other weak forces govern the organization of multicomponent supramolecular assemblies.[3] A deep understanding of these interactions is of outstanding importance for the rationalization of effects observed in several fields, such as biochemistry and materials science. A quantitative description of these interactions can be performed taking advantage of quantum chemical calculations on small model systems.[4] The interplay of theory and experiment in many fields has been very productive, in particular for the elucidation of molecular structures and for the comprehension of chemical binding, being an ideal link between theory and experiment.

1,2,4,5-Tetrazines, the most nitrogen-rich six-membered aromatic heterocycles (Scheme 1), are exceptional species either in organic, metal–organic[5] or materials chemistry.[6] The unique properties of tetrazines originate in their extreme electron deficiency, which is responsible for a high reactivity of tetrazines as azadienes in the inverse electronically demanding Diels–Alder reaction and [4 + 1] cycloadditions allowing versatile synthetic pathways for a number of compounds such as pyridazines, triazines, pyrroles, pyrazoles and condensed heterocycles.[7,8] The electron deficiency of the π-system was also a prerequisite for the ability of tetrazines to sustain efficient attraction with negatively polarized atoms or anions, a type of interaction that was only clearly recognized recently.[9] In view of coordination chemistry, the very low energy of the π* orbital localized at the four nitrogen atoms predetermines a strong interaction in tetrazine-bridged mixed-valent compounds.[10] This may be applicable in the development of electroconducting metal–organic polymers, especially taking into account the availability of multiple binding sites of the ligands and their potential for bridging many metal ions and generation of complicated framework architectures.[5]



Scheme 1 1,2,4,5-Tetrazine ligands explored in the present study.

However, whether the tetrazines could be exploited as tetradentate N-donors towards typical metal ions, was an enigma. These

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low-basic (p$K_{\mathrm{BH}^+} < 0$)[11] species are relatively weak σ-donors and in all previously reported compounds they utilize only a part of the available coordination functionality as monodentate or *trans*-bidentate bridging groups.[5,12] In this present contribution we report a series of new coordination compounds involving either the parent unsubstituted 1,2,4,5-tetrazine (ttz) or its 3,6-dimethyl derivative (Me_2ttz) (Scheme 1), which illustrate the real potential of tetrazines as very efficient multidentate ligands for coordination chemistry. We also report a high level *ab initio* study where we explore the binding ability of 1,2,4,5-tetrazine itself toward anions and how it is affected by the progressive N-coordination with two and four silver(I) ions.

Results and discussion

In all of the examined silver(I) and copper(I) compounds the ligands adopt an unprecedented μ_4-coordination only, which thus may be regarded as a typical and well-predictable feature of the system. This may be related to the more common coordination chemistry of 1,3,5-triazine that in fact reveals only a scarce number of examples for complete μ_3-coordination.[13,14] For providing such an unusual μ_4-donor capacity, the electronic factors could be particularly prevalent and the ability of very soft d^{10}-metal ions (Cu^+, Ag^+) for π back-donation may be involved as a key factor for their high affinity towards heterocyclic N-donors,[15] now including even extreme electron deficient tetrazines.

The 3D coordination frameworks of [Ag(ttz)(X)] (X = NO_3 **1**; ClO_4 **2**) are very similar and they are especially illustrative for the coordinating ability of the ligand, since the silver ions bind to four tetrazine-N donors (Ag–N 2 × 2.424, and 2 × 2.486 Å (**1**), and 4 × 2.526 Å in **2**) and one terminal O-donor counter anion (Ag–O 2.431–2.537 Å) (Table 1). Thus both the metal ions and the μ_4-tetrazine ligands provide topologically equivalent four-connected nodes for the overall 3D framework linkage, which results in the form of the rarely encountered net $\{4^2;8^4\}$ (three-letter notation "lvt").[16] The metal–tetrazine framework is adaptable to the steric volume of counter anions and in **1** and **2** it solely occupies 81.0 and 68.9% of the space,[17] respectively, thus allowing the situation of either nitrate or larger perchlorate anions inside the channels running along the *a* direction (Fig. 1). Four-fold AgN_4 coordination in these structures may be compared with the behavior of silver ions towards 1,3,5-triazine. In that case, preparation of the coordination compounds was difficult[14] and the products adopting AgN_3 or AgN_3 + AgN_4 types of the metal environment (Ag–N 2.28–2.67 Å) could be isolated only with weakly nucleophilic anions (BF_4^-, $CH_3SO_3^-$).[14] Even more close structural analogy is demonstrated by bicyclic pyridazino[4,5-*d*]pyridazine,[18] which commonly affords AgN_4 to AgN_6 types of coordination.

Table 1 Selected bond distances (Å) and angles (°) for complexes **1** and **2**

$[Ag(ttz)(NO_3)]$ **1** (a: x, $1.5 - y$, z; b: $x + 0.5$, y, $0.5 - z$; c: $x + 0.5$, $1.5 - y$, $0.5 - z$)			
Ag1–N1	2.4242(18) × 2	N1–Ag1–N1a	97.47(9)
Ag1–N2	2.4857(19) × 2	N1–Ag1–N2b	85.59(6)
Ag1–O1	2.431(5) × 2	N1–Ag1–N2c	162.93(8)
N1–Ag1–O1	88.08(16)		
$[Ag(ttz)(ClO_4)]$ **2** (a: $0.5 - x$, y, $0.5 - z$; b: x, $1.5 - y$, z; c: $0.5 - x$, $1.5 - y$, $0.5 - z$)			
Ag1–N1	2.526(4) × 4	N1–Ag1–N1a	94.22(17)
Ag1–O3[a]	2.54(2)	N1–Ag1–N1b	85.78(17)
Ag1–O4A[a]	2.45(2)	O4A–Ag1–N1	84.8(5)
O4A–Ag1–N1c	95.2(5)		

[a] O3 and O4A correspond to two orientations of the disordered anion.

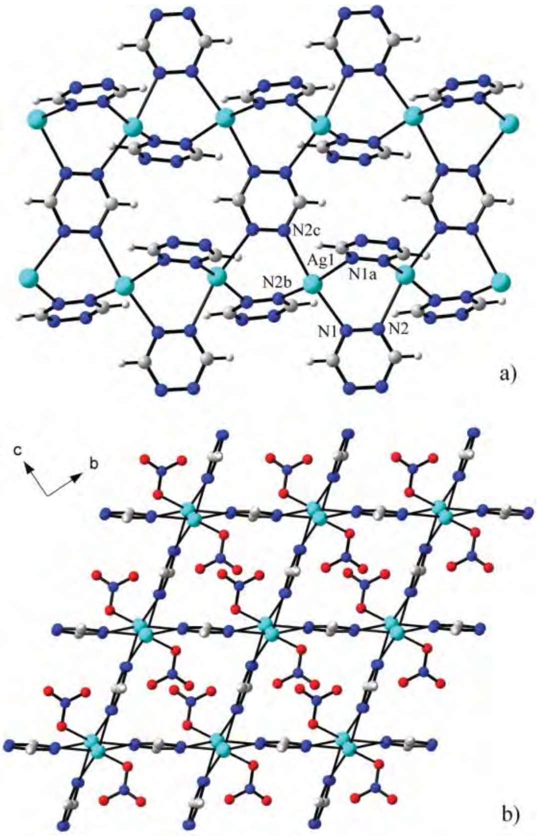


Fig. 1 (a) Metal–organic motif in the structures of **1** and **2** showing how the chains of the Ag ions are interconnected in two orthogonal directions by μ_4-tetrazine bridges. (b) View of the framework in **1** along the direction of the channels providing the accommodation of the coordinated NO_3^- ions.

Substitution at the ligand frame had an impact on the structure as was revealed by complexes of 3,6-dimethyltetrazine. The increased steric volume of the ligand and the presence of methyl groups in α-positions to the donor atoms resulted in coordination of only two tetrazine molecules to each metal ion in $[Ag_2(Me_2ttz)(NO_3)_2]$ **3** and $[Ag_2(Me_2ttz)(H_2O)_2(ClO_4)_2]$ **4** (Fig. 2), combination of 1 : 2 and 1 : 1 coordinations in $[Ag_3(Me_2ttz)(H_2O)_2(CF_3SO_3)_3]$ **5** and 1 : 1 coordination in $[Cu_4Cl_4(Me_2ttz)]$ (**6**). However, even the substitution does not mitigate against the binding of many metal ions to tetrazine and in all the compounds the ligand retains the μ_4-coordination mode.

For **3** and **4** this results in the formation of 1D disilver–tetrazine ribbons as a clearly distinguishable basic motif of the structure (Fig. 2), with very similar Ag–N bond lengths in a range of 2.3577(16)–2.4504(17) Å. In **3**, these ribbons were further interconnected by nitrate anions, which form a pair of equal Ag–O bonds (2.51 and 2.54 Å) and two longer contacts at 2.63 and

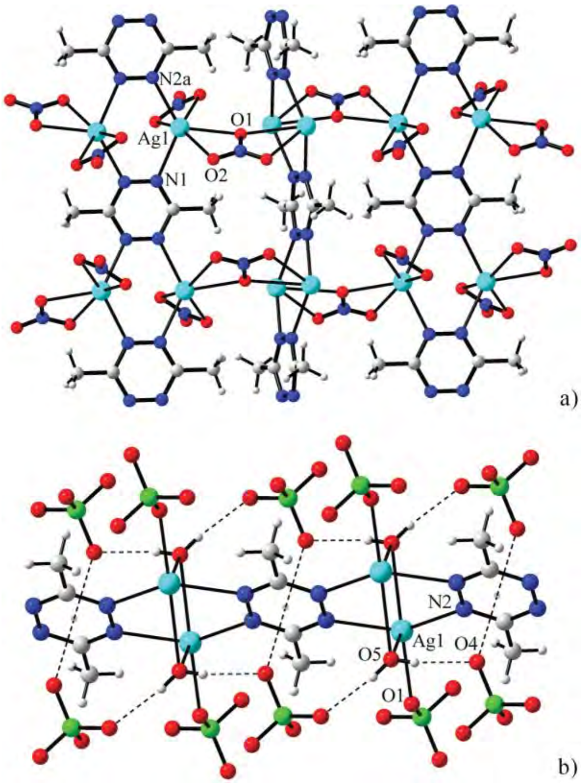


Fig. 2 (a) Fragment of the structure of **3** demonstrating the interconnection of the [Ag_2(μ_4-tetrazine)] chains by bridging nitrate anions. (b) Similar motif of the structure of **4** with coordinating ClO_4^- anions. Note the combination of coordination and hydrogen bonding with the close and directional anion···π interaction at either side of the tetrazine cycle (O···π 2.818(4) Å).

2.70 Å completing a distorted octahedral six-coordination around metal ions.

In perchlorate complex **4**, each dimeric silver–tetrazine unit accommodates water molecules at both axial sides simultaneously, which provide very long bridges between the silver ions (Ag–O 2.64, 2.77 Å). The ribbons are linked by bridging perchlorate anions (Ag–O 2.51, 2.59 Å) and a set of hydrogen bonding. The structure of **5** is essentially ionic and it is dominated by assembly of the double chains composed with silver and triflate ions and bridging water molecules (Ag–O 2.369(10)–2.538(9) Å), while the μ_4-tetrazine molecules interconnect this chains into a 3D framework (with the Ag–N bond lengths in the range 2.38–2.57 Å) (Fig. 3, Table 2).

The efficient donor ability of tetrazine was further illustrated by a copper(I) chloride complex. Unlike most of the silver compounds involving weakly coordinating anions, the structure of [$Cu_4Cl_4(Me_2ttz)$] (**6**) demonstrates interplay of the nucleophilic chloride and tetradentate tetrazine ligands for supporting 3D architecture. Inorganic linkage itself is unprecedented and it exists as 2D corrugated layers composed of copper(I)–chloride four-, six- and octagons (in a 1 : 2 : 1 proportion) (Fig. 4). The tetrazine ligands bridge pairs of the adjacent metal ions (completing their typical tetrahedral environment $CuNCl_3$) within the octagonal units and thus they connect successive layers and expand the structure in a third direction (Fig. 4). Separations of Cu–N are actually uniform (1.974(2) and 1.981(2) Å) (Table 3) and they are even shorter than in comparable copper(I) chloride complexes with pyridazine (1.99–2.03 Å)[19] or copper(I) bromide complex involving μ_3-1,3,5-triazine (2.075 Å).[20]

Table 2 Selected bond distances (Å) and angles (°) for complexes **3–5**

[$Ag_2(Me_2ttz)(NO_3)_2$] **3** (a: 1 − x, 1 − y, −z)			
Ag1–N1	2.4504(17)	N2a–Ag1–N1	128.39(6)
Ag1–N2a	2.3577(16)	N2a–Ag1–O1	123.96(6)
Ag1–O1	2.5113(18)	N1–Ag1–O1	107.64(6)
Ag1–O2	2.5378(18)	N2a–Ag1–O2	128.15(6)
N1–Ag1–O2	84.10(6)		
O1–Ag1–O2	50.71(6)		
[$Ag_2(Me_2ttz)(H_2O)_2(ClO_4)_2$] (**4**) (a: −1 + x, y, z; b: 1 − x, 1 − y, −z)			
Ag1–N2a	2.375(2)	N2a–Ag1–N1	132.50(8)
Ag1–N1	2.431(2)	N1–Ag1–O1	108.29(9)
Ag1–O1	2.507(2)	N1–Ag1–O3b	87.87(8)
Ag1–O3b	2.590(3)	O1–Ag1–O3b	82.65(9)
Ag1–O5	2.638(3)	N2a–Ag1–O5	75.20(8)
N1–Ag1–O5	76.32(8)		
O1–Ag1–O5	93.82(9)		
[$Ag_3(Me_2ttz)(H_2O)_2(CF_3SO_3)_3$] (**5**) (a: 1 + x, y, z; b: −x, −0.5 + y, 0.5 − z)			
Ag–O	2.369(10)–2.538(9)	Ag4–N7	2.514(7)
Ag1–N1	2.380(7)	Ag5–N6	2.567(8)
Ag1–N8a	2.408(8)	Ag6–N3	2.379(7)
Ag2–N2	2.549(8)		
Ag3–N4b	2.394(8)	N1–Ag1–N8a	126.1(2)
Ag3–N5	2.426(8)	N4b–Ag3–N5	129.7(3)

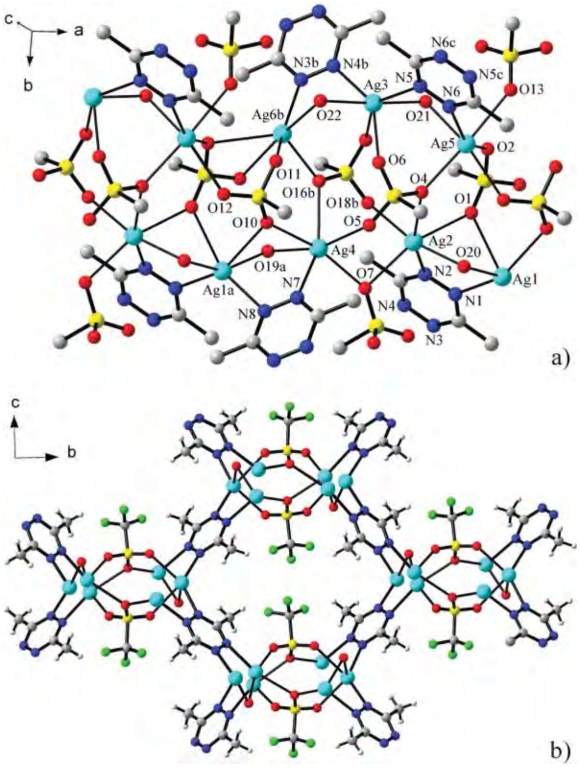


Fig. 3 (a) Structure of **5**, showing aquasilver–triflate chains accommodating tetrazine ligands. (b) Projection of the structure along the direction of silver–triflate chains. Integration of the chains into the 3D framework occurs by means of μ_4-tetrazine bridges.

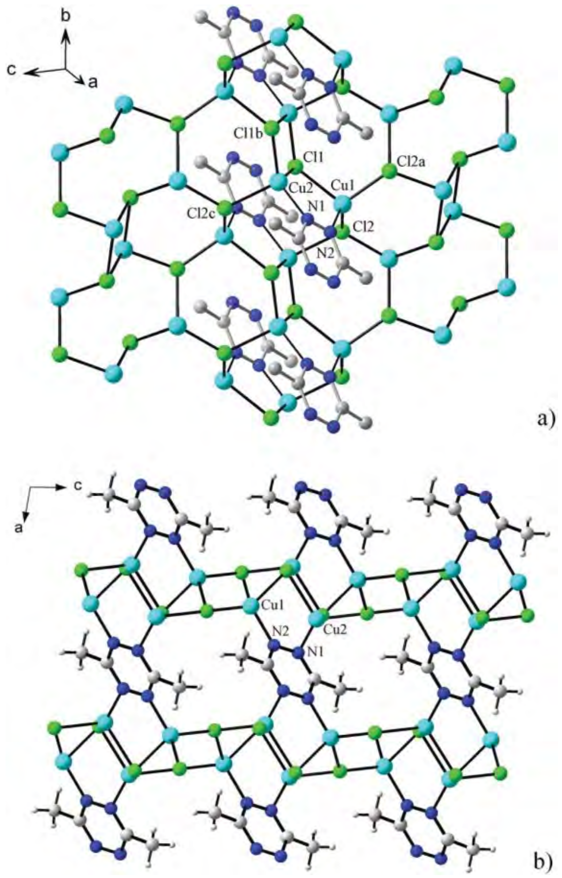


Fig. 4 (a) Structure of a copper chloride layer in the structure of **6**, showing mode of interaction with tetrazine molecules at both axial sides of the layer. (b) Function of tetrazine as μ_4-bridges between the successive layers of the structure.

Geometry of the 1,2,4,5-tetrazine ring

Table 3 Selected bond distances (Å) and angles (°) for complex **6**[a]

Cu1–N2	1.974(2)	Cu2–N1	1.981(2)
Cu1–Cl2a	2.2925(8)	Cu2–Cl1b	2.2965(8)
Cu1–Cl2	2.3514(8)	Cu2–Cl2c	2.3718(8)
Cu1–Cl1	2.4283(8)	Cu2–Cl1	2.4442(8)
N2–Cu1–Cl2a	116.15(7)	N1–Cu2–Cl1	108.71(7)
N2–Cu1–Cl2	115.99(7)	Cl1–Cu2–Cl1b	97.87(3)
Cl2–Cu1–Cl2a	111.10(2)	Cl1–Cu2–Cl2c	109.02(3)
N2–Cu1–Cl1	108.15(7)	Cu2b–Cl1–Cu1	125.70(3)
Cl2–Cu1–Cl1	95.87(3)	Cu1–Cl1–Cu2	82.90(3)
N1–Cu2–Cl1b	130.71(7)	Cu1–Cl2–Cu2c	103.58(3)
N1–Cu2–Cl2c	101.31(7)		

[a] Symmetry codes: a: −*x*, 0.5 + *y*, 1.5 − *z*; b: −*x*, 1 − *y*, 2 − *z*; c: −*x*, −*y*, 2 − *z*.

The main parameters of the ring, such as C–N and N–N bond lengths (Table 4) are in good agreement with the parameters for non-coordinated ttz[21] and Me_2ttz[22] molecules and for Cu(II) complexes with very distal axial Cu–N coordination.[12c] This suggests the absence of a significant electron transfer in the system, unlike complexes of Ru(II) and Ti(II) involving μ-ttz ligands. In the latter case, lengthening of N–N bonds and loss of planarity were indicative even, of reduction of tetrazine and the formation of Ti(III) complex with ttz anion radical.[12a] In most of the examined structures the tetrazine molecules are exactly planar and situated across a center of inversion. However, in **3** the aromatic ring is somewhat distorted and it exhibits 9.5(3)° bent along the C–C axis.

Anion···π interactions of 1,2,4,5-tetrazine

Since the high π-acidity of tetrazines results in attractive interactions with negatively polarized atoms,[9] the multiple N-coordination to metal ions as Lewis acids may be a factor influencing the LUMO energy and enhancing the ability of the aromatic tetrazine system for anion···π binding. This was applicable for complexes of the unsubstituted tetrazine **1** and **2**, which exhibit very efficient interactions of this type with corresponding O···C(N) separations down to 2.78 Å, at both axial sides of the aromatic ring simultaneously. Thus, each of the coordinated nitrate (perchlorate) anions sustains short contacts with the aromatic frame at the adjacent wall of the framework

Table 4 Geometry of 1,2,4,5-tetrazines in crystal structures

Compound	Symmetry	C–N/Å	N–N/Å	∠CNN/°
1,2,4,5-Tetrazine				
(**1**)	$\bar{1}$	1.331(3), 1.332(3)	1.320(3)	117.3(2), 117.4(2)
(**2**)	2/*m*	1.337(5)	1.333(8)	117.1(3)
ttz[21]	$\bar{1}$	1.323, 1.347	1.327	116.3, 116.5
$[Ti^{II}Cp_2(\mu\text{-ttz})]_4$[12a,a]	1	1.298–1.378	1.412, 1.421	110.3, 110.9; 114.0, 116.2
$[\{Ru^{II}(NH_3)_5\}_2(\mu\text{-ttz})](BPh_4)_4$[12b]	$\bar{1}$	1.315, 1.371	1.387	113.8, 117.6
$Cu^{II}\{CF_3COCHCOCF_3\}(ttz)$[12c]	1	1.305–1.336	1.304, 1.329	116.4–116.8
3,6-Dimethyl-1,2,4,5-tetrazine				
(**3**)[a]	*m*	1.345(2), 1.349(2)	1.324(2)	118.5(2), 119.1(2)
(**4**)	$\bar{1}$	1.342(3), 1.345(3)	1.326(3)	118.7(2), 118.8(2)
(**5**)	$\bar{1}$	1.34(1), 1.36(1)	1.33(1)	118.1(8), 119.4(8)
	$\bar{1}$	1.35(1), 1.36(1)	1.31(1)	118.0(8), 118.8(8)
	1	1.34(1)–1.36(1)	1.32(1), 1.33(1)	117.8(9)–118.4(9)
(**6**)	$\bar{1}$	1.345(4), 1.347(4)	1.346(3)	118.1(2), 118.3(2)
Me_2ttz[22]	$\bar{1}$	1.334, 1.343	1.326	117.9, 118.1

[a] Aromatic frame is essentially non-planar.

channel and therefore the arrangement of the O···π interaction is also influenced by coordination of the anion to the metal center.

In **1**, the relatively efficient Ag–ONO$_2$ coordination (Ag–O 2.431 Å) mitigates against very strong anion···π bonding, which is comparable with F···π interactions in hexafluoroarsenate complexes of 3,6-bis(2-pyridyl)tetrazine (F···π 2.80–3.04 Å).[23] However, present O···π distance (2.98 Å, Table 4) is the shortest contact observed for the nitrate ion and 1,2,4,5-tetrazines, as revealed by a comprehensive CSD study (O···π mean 3.16 Å).[24] Weaker coordination of the ClO$_4^-$ anions in **2** (Ag–O 2.537 Å) facilitates their closest contact to the π-acidic tetrazine (Fig. 5). In this sense, the coordination and anion···π interactions are competitive and equally important for the position of the perchlorate anion, which exhibits exceptionally short O···π separations (with O···plane distances approaching 2.58 Å and O···centroid distances 2.61 and 2.76 Å) (Table 5). The precedents for anion···π stacking involving low nucleophilic ClO$_4^-$ anions was recently found for the triazine system[25] and also for a complex with a condensed pyridazino[4,5-*d*]pyridazine,[8] with significantly longer O···π distances at 2.94 and 3.05 Å, respectively. The observed interaction may be evaluated as quite strong by comparison with the results of the CSD study (O···π mean 2.91 Å).[24]

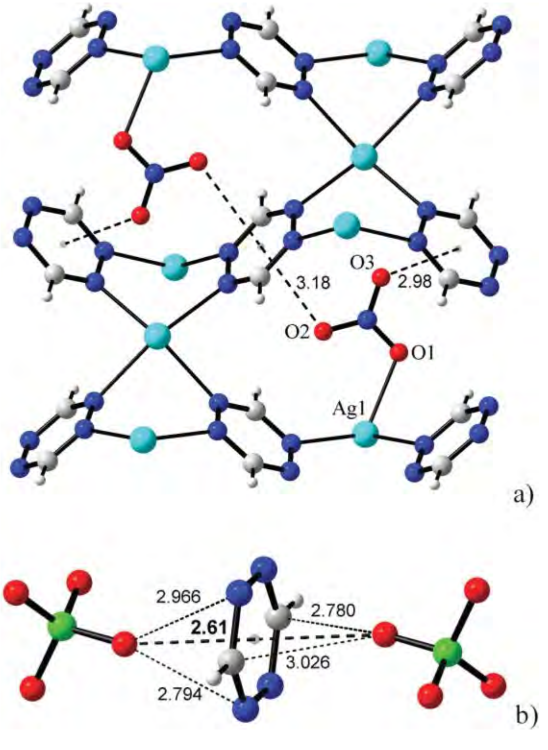


Fig. 5 Short directional anion···π interactions observed in the structures of **1** (a) and **2** (b). The tetrazine frame maintains equally effective contacts with the ClO$_4^-$ anions at both axial sides.

Competition of coordination and anion···π attraction is relevant also for a series of 3,6-dimethyltetrazine compounds, where the multiple Ag–nitrate interactions are responsible for the elimination of direct O···π interactions, while in [Ag$_2$(Me$_2$ttz)(H$_2$O)$_2$(ClO$_4$)$_2$] **4**, the oxygen atom of a perchlorate anion is situated almost exactly above the centroid of tetrazine ring with an appreciably short O···π distance of 2.818(4) Å (Fig. 2). In the structure of **5**, one of the triflate anions also exhibits short contact of this type (with O···π and O···plane distances at 2.923(8) and 2.712(9) Å, respectively), while another such interaction proceeds through the electronegative fluorine atom of the CF$_3$ group (F···π 3.043(8) Å) (Table 5). This "lone pair-aromatic" CF$_3$···π stacking[26] is also notably short and it agrees with the parameters for RF···1,3,5-triazine interactions found from a CSD analysis (F···π mean 3.01 Å),[27] while only two precedents for RF···1,2,4,5-tetrazine contacts were even somewhat longer (3.18 Å).[27]

Table 5 Geometry of the anion···π interactions with tetrazine

Complex	Atom (X)	X–C(N) range/Å	X···centroid distance/Å	X···plane distance/Å	φ/°[a]
1	O	2.81–3.68	2.982(5)	2.797(5)	69.8
	O	3.21–3.68	3.180(7)	3.117(6)	78.6
2	O	2.78–3.09	2.611(9)	2.587(9)	82.2
	O	2.84–3.31	2.764(10)	2.708(9)	78.4
4	O	2.99–3.25	2.818(4)	2.802(4)	83.9
5	O	2.76–3.63	2.923(8)	2.712(9)	68.1
	F	3.24–3.41	3.043(8)	3.036(9)	86.1
6	Cl	3.18–3.92	3.300(2)	3.147(2)	72.5

[a] Angle of the O···π axis to the plane of the aromatic cycle.

Anion···π interactions are also essential for chloride complex **6** although the rigid structure of the Cu–Cl linkage evidently does not allow the close situating of the tetrazine ring and chloride ions. However, this contact is directional and it nearly completes a tetrahedral environment of chloride ions (with the Cu–Cl1···π angles 116.2–118.9°) (Fig. 6). Corresponding Cl···π separation (3.300(2) Å) agrees well with the calculated equilibrium distance for Cl$^-$···1,3,5-triazine system (3.20 Å).[28]

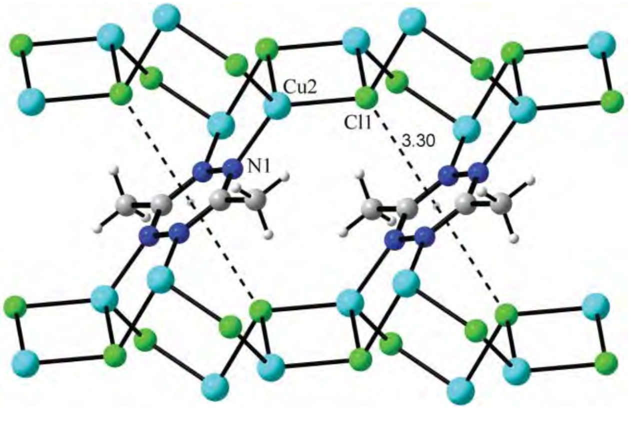
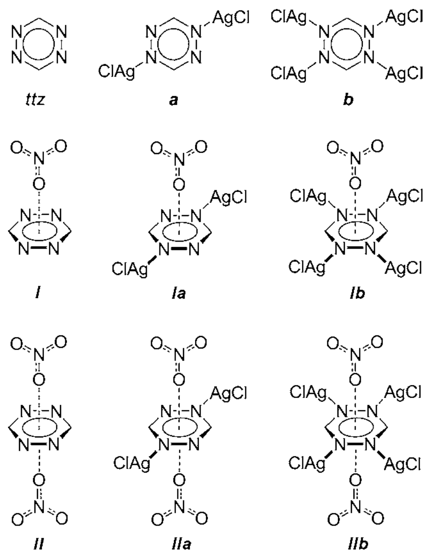


Fig. 6 Directional Cl···π interactions in the structure of **6**. Note the actually tetrahedral environment of the Cl1 atoms, which include three Cu ions and π-system.

Theoretical study

In order to evaluate how the coordination of tetrazine to Ag(I) ions could influence the anion-binding properties of the aromatic ring we have used high level *ab initio* calculations allowing the comparison of the anion complexes of ttz and its silver derivatives (**a**) and (**b**) with NO$_3^-$, see Scheme 2. The presence of Ag(I) coordinated to the nitrogen atom increases the π-acidity of the aromatic ring and the anion···π complexes are more favored with



Scheme 2 Computational models of 1,2,4,5-tetrazine complexes.

respect to the interaction of anions with uncoordinated ttz. In the model compounds (**a**) and (**b**), we have used chloride as the counter ion of Ag(I) in order to keep the model neutral, allowing a direct comparison with ttz.

The complexation energies and equilibrium distances obtained at the RI-MP2(full)/auc-cc-pVTZ//RI-MP2(full)/TZVP level of theory are summarized in Table 6. From the examination of the results, several interesting points arise. Firstly, the interaction energy of binary complexes **I–Ib** is negative indicating a favorable interaction. The presence of silver(I) attached to the aromatic ring drastically changes the anion-binding properties of the tetrazine ring. For instance, when ttz is coordinated to two silver(I) atoms, it is able to form an anion–π complex with NO_3^- (**Ia**) with a computed binding energy of –127.2 kcal mol^{-1}, more than ten times more favorable than ttz. The binding energy computed for **Ib** is –62.35 kcal mol^{-1}, which is also much more negative than the one computed for ttz, however it is less favorable than the binding energy of **Ia**.

This unexpected result is due to the decrease of aromaticity of the tetrazine ring provoked by the deformation of the ring in complex **Ib**, as can be appreciated in the representation of Fig. 7. This finding perfectly complements the experimental geometry of the tetrazine ligand in complex **3**. However, in the other compounds the tetrazine molecules are situated across a center of inversion and their aromatic frames are planar.

Table 6 Interaction energies without and with the BSSE correction (E and E_{CP} respectively) and equilibrium distances (R_e) computed for complexes **I–IIb**[a]

Complex	E/kcal mol^{-1}	E_{CP}/kcal mol^{-1}	R_e/Å
I	−10.81	−9.63	2.562
Ia	−130.33	−127.17	2.371
Ib	−67.53	−62.35	2.262
II	26.96	27.57	3.027
IIa	−3.10	2.45	2.522
IIb	−20.20	−11.55	2.598

[a] RI-MP2/TZVP//RI-MP2/aug-cc-pVTZ level of theory.

Secondly, the equilibrium distance of binary complexes **I–Ib** decreases as the number of silver atoms coordinated to tetrazine increases (Fig. 7), indicating a progressive enhancement of the anion···π bonding. Thirdly, the results obtained for the ternary complexes **II–IIb** are very relevant and illustrative. They indicate that the simultaneous interaction of tetrazine with two NO_3^- anions is very repulsive (27.57 kcal mol^{-1}, complex **II**). When the tetrazine ring is coordinated to two silver atoms (complex **IIa**), the binding energy for the simultaneous interaction with two NO_3^- turns out to be 2.45 kcal mol^{-1}. Bearing in mind that the optimization of the complex is carried out in the gas phase and that two negative charges are present in the complex, we can conclude that the effect of having two silver atoms coordinated to tetrazine upon the π-acidity of the ring allows a simultaneous interaction with two anions. As a matter of fact, a spectacular shortening of the equilibrium distance (0.5 Å) is observed in complex **IIa** with respect to **II**, see Fig. 8. The most important finding is the geometrical and energetic features obtained for complex **IIb**. The binding energy is negative (–11.55 kcal mol^{-1}) and the equilibrium distance is short (2.598 Å). This very short equilibrium distance is in agreement with the experimental distance observed in the crystal structure of **2** (2.61 Å see Fig. 5(b)), which is the shortest anion···π distance observed to date. In the X-ray structures **1** and **6**, this recognition pattern (anion···π··· anion) is also observed, see Fig. 5 and 6. The equilibrium distances are larger, because the anion that participates in the anion···π contact is also coordinated to the transition metal.

Conclusions

The reported compounds provide exceptional precedents for the functional properties of the 1,2,4,5-tetrazine system, either as N-donor for coordination chemistry or π-acidity for sustaining

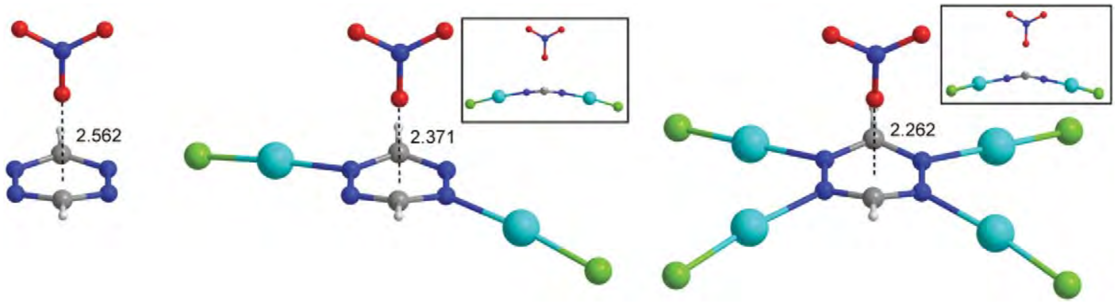


Fig. 7 The optimized binary complexes **I–Ib** of tetrazine derivatives and nitrate anion are shown. Distances are in Å.

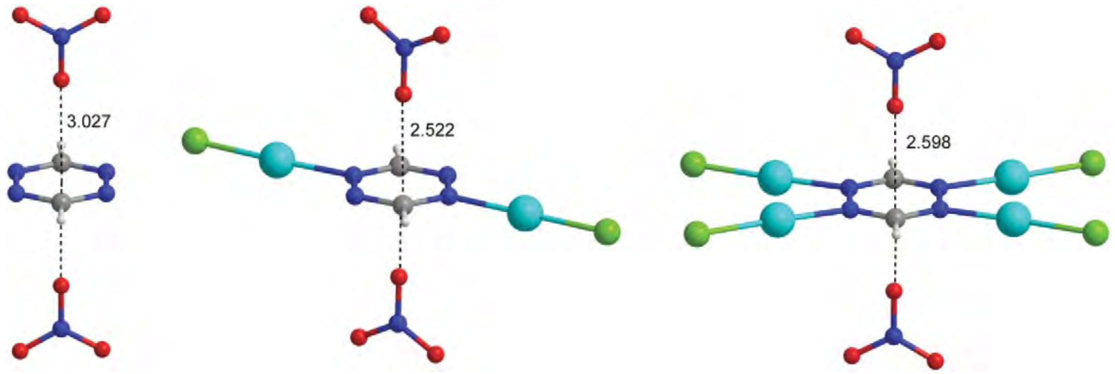


Fig. 8 The optimized ternary complexes **II–IIb** of tetrazine derivatives and nitrate are shown. Distances are in Å.

very short interaction with anions. This may find further applications in the development of novel metal–organic molecular or framework materials capable of electric conductivity, for evaluation of novel types of interactions, for design of systems for anion hosting, recognition and sensing[29] as well as for the modelling of cycloaddition reactions of tetrazine. The theoretical study demonstrate the important enhancement of the π-acidity of the tetrazine ring when it is coordinated to silver(I) atoms, allowing the favorable and simultaneous interaction with two anions even in the gas phase. A good agreement with the experimental results is observed.

Experimental

Synthesis

Prior to the preparation of coordination compounds, the tetrazine ligands ttz[30a] and Me_2ttz[30b] were freshly purified by sublimation. All the coordination compounds were intensive colored crystalline materials, relatively stable in air. Crystallization of the ttz complexes was commonly accompanied by a partial reduction of metal ions and formation of a silver mirror. With silver trifluoroacetate and hexafluorophosphate, the reduction occurs within minutes thus precluding isolation of the products. However, the nitrate and perchlorate complexes (**1** and **2**) were readily prepared in methanolic solutions, while reaction of the components in water led to immediate and quantitative precipitation of silver metal.[31]

Preparation of [Ag(ttz)(NO_3)] (1), [Ag_2(Me_2ttz)(NO_3)$_2$] (3) and [Cu_4Cl_4(Me_2ttz)] (6)

A solution of 1,2,4,5-tetrazine (24.6 mg, 0.3 mmol) in 2 ml methanol was layered over a solution of $AgNO_3$ (17.0 mg, 0.1 mmol) in 3 ml of a 1 : 1 v/v mixture of methanol and chloroform. Large deep-violet crystals of the product **1** grew on the walls of the tube as the solutions inter diffused over a period of 15 d. The yield was 14 mg (55%). The compound is unstable under the mother liquid and is light-sensitive. Starting with 3,6-dimethyltetrazine, complex **3** was prepared as red-violet prisms, while complex **6** (black prisms) was prepared in a similar fashion using a solution of CuCl in anhydrous acetonitrile.

Anal. for **1**, $C_2H_2AgN_5O_3$. Calc. (%): C, 9.53; H, 0.80; N, 27.80. Found (%): C, 9.22; H, 0.61; N, 27.56. Anal. for **3**, $C_4H_6Ag_2N_6O_6$. Calc. (%): C, 10.68; H, 1.34; N, 18.68. Found (%): C, 10.37; H, 1.22; N, 18.21. Anal. for **6**, $C_4H_4Cl_4Cu_4N_4$. Calc. (%): C, 9.49; H, 1.20; N, 11.07. Found (%): C, 9.07; H, 1.12; N, 10.58.

Preparation of [Ag(ttz)(ClO_4)] (2) and [Ag_2(Me_2ttz)(H_2O)$_2$(ClO_4)$_2$] (4)

A solution of 1,2,4,5-tetrazine (32.8 mg, 0.4 mmol) and $AgClO_4\cdot H_2O$ (45.1 mg, 0.2 mmol) in 3 ml methanol was filtered and then slowly evaporated in a vacuum desiccator over $CaCl_2$ yielding 28 mg (45%) of deep-violet prisms of the complex. Starting with Me_2ttz ligand, complex **4** was prepared as red blocks.

Anal. for **2**, $C_2H_2AgClN_4O_4$. Calc. (%): C, 8.30; H, 0.70; N, 19.36. Found (%): C, 8.01; H, 0.52; N, 18.98. Anal. for **4**, $C_4H_{10}Ag_2Cl_2N_4O_{10}$. Calc. (%): C, 8.57; H, 1.80; N, 9.99. Found (%): C, 8.29; H, 1.77; N, 9.54.

Theoretical methods

The geometries of all complexes studied in this work were fully optimized at the RI-MP2/TZVP level of theory using the Turbomole program.[32] These geometries were used to perform single point calculations using the augmented correlation-consistent polarized valence triple-ζ (aug-cc-pVTZ) basis set in order to obtain more accurate energetic values. For the silver atom the calculations were performed using a relativistic effective core potential (ECP28MWB).[33] The binding energies were calculated with correction for the basis set superposition error (BSSE) by using the Boys–Bernardi counterpoise technique.[34]

Crystallography

Crystallographic measurements were made using a Stoe Imaging Plate Diffraction System (213 K, Mo Kα radiation, $\lambda = 0.71073$ Å, numerical absorption corrections using X-RED and X-SHAPE).[35] The structures were solved by direct methods using the program SHELXS-97.[36] The refinement and all further calculations were carried out using SHELXL-97.[36] The non-H atoms were refined anisotropically, using weighted full-matrix least-squares of F^2 (Table 7). For **1**, the hydrogen atoms were located and refined isotropically, while for **4** the hydrogen atoms of water molecule were located and then fixed. For all other structures the hydrogen atoms were added geometrically. In structure **1**, the nitrate anion was equally disordered over two positions related by a mirror plane. It was possible to refine this group anisotropically and without any restraints in geometry. The perchlorate anion in

Table 7 Crystal data for [Ag(ttz)(NO_3)] (**1**), [Ag(ttz)(ClO_4)] (**2**), [Ag_2(Me_2ttz)(NO_3)$_2$] (**3**), [Ag_2(Me_2ttz)(H_2O)$_2$(ClO_4)$_2$] (**4**), [Ag_3(Me_2ttz)(H_2O)$_2$(CF_3SO_3)$_3$] (**5**) and [Cu_4Cl_4(Me_2ttz)] (**6**)

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_2H_2AgN_5O_3$	$C_2H_2AgClN_4O_4$	$C_4H_6Ag_2N_6O_6$	$C_4H_{10}Ag_2Cl_2N_4O_{10}$	$C_{14}H_{20}Ag_6F_{18}N_8O_{22}S_6$	$C_4H_6Cl_4Cu_4N_4$
T/K	213	213	213	213	213	296
M	251.96	289.40	449.89	560.80	1833.96	506.09
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	*Pnma*	*Imma*	*Pnma*	$P\bar{1}$	$P2_1/c$	$P2_1/c$
Z	4	4	4	1	4	2
a/Å	7.7351(7)	8.4650(7)	9.0359(8)	6.7481(8)	10.5847(9)	6.8143(9)
b/Å	10.8172(8)	10.4250(11)	13.2071(13)	7.9981(9)	19.0579(13)	6.2582(8)
c/Å	7.1540(6)	7.7750(6)	8.7513(7)	8.1382(10)	23.1327(14)	13.6220(17)
β/°				65.663(10)[a]	102.038(10)	98.907(4)
U/Å^3	598.59(9)	686.13(11)	1044.36(16)	349.00(8)	4563.8(6)	573.91(13)
μ(Mo Kα)/mm^{-1}	3.328	3.306	3.785	3.247	2.956	8.210
D_c/g cm^{-3}	2.796	2.802	2.861	2.668	2.669	2.929
$2\theta_{max}$/°	56.4	56.3	55.8	56.0	51.4	53.1
Meas/unique reflections	4180/762	1878/473	7298/1291	3380/1662	19171/8501	1968/1155
R_{int}	0.043	0.028	0.071	0.037	0.056	0.018
Parameters refined	71	55	88	100	671	75
R_1, wR_2 [$I > 2\sigma(I)$]	0.019, 0.044	0.033, 0.084	0.021, 0.050	0.029, 0.071	0.078, 0.187	0.023, 0.056
R_1, wR_2 (all data)	0.022, 0.045	0.045, 0.088	0.031, 0.052	0.031, 0.071	0.121, 0.206	0.027, 0.057
Max, min peak/e Å^{-3}	0.54, −0.87	0.69, −0.49	0.48, −0.70	1.21, −1.19	3.25, −2.69	0.63, −0.72

[a] $\alpha = 65.302(11)°$, $\gamma = 66.151(11)°$.

structure **2** was also disordered, with the Cl atom lying on the intersection of two mirror planes, while the ClO_4 tetrahedra adopt two independent orientations. In total this affords disordering of the oxygen atoms over eight positions. The disorder was readily resolved and refined with a set of soft restraints for geometry of ClO_4, the ordered Cl atom was refined anisotropically and the oxygen atoms were left isotropic. Attempted refinement of the structure in the space groups of lower symmetry (*cf.* $C2/m$) did not provide improvements for the disordering scheme. The high residual electron density near three of six independent silver ions (at 0.40–0.70 Å) in **5** suggested possible twinning. However, refinement in space groups of lower symmetry was not successful. In this structure, relatively high anisotropy for thermal motion of F atoms was indicative of the disorder. We were not successful to resolve it. Graphical visualisation of the structures was made using program Diamond.[37] CCDC reference numbers 679092–679096 and 705413.†

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