Copper(I) and silver(I) coordination frameworks involving extended bipyridazine bridges

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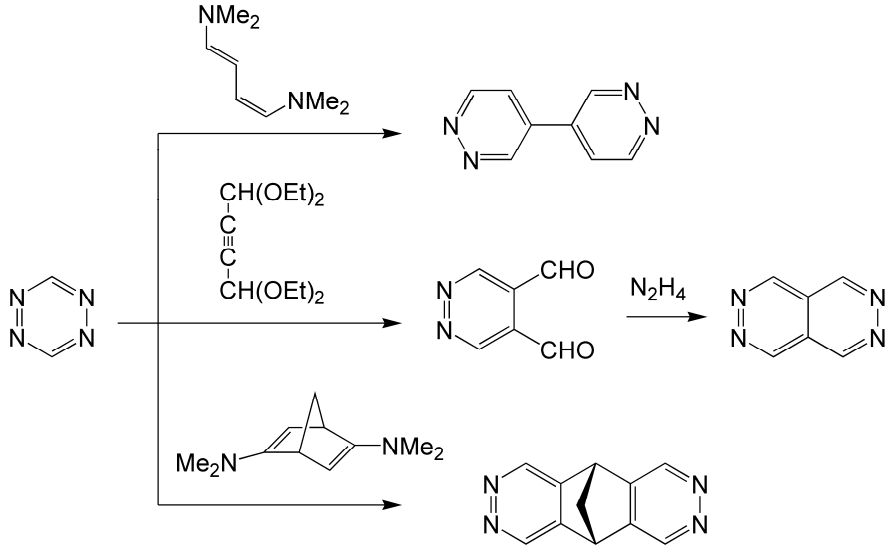
Preparation of 1,2,4,5-tetrazine.

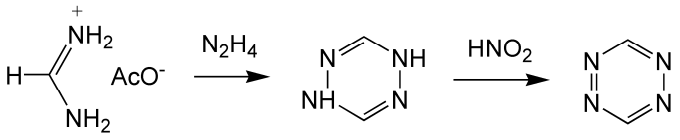
Unsubstituted 1,2,4,5-tetrazine is a valuable starting compound for “inverse electron demand Diels-Alder cycloadditions” allowing preparation of a range of pyridazine, triazine, pyrrole, pyrazole compounds and of condenced polycycles. Recent literature concerning reactions of tetrazine derivatives were reviewed (N. Saracoglu, *Tetrahedron*, 2007, **63**, 4199). Tetrazines are also exceptional species for coordination chemistry, supporting very strong coupling of metal ions in bridged mixed-valence species (W. Kaim, *Coord. Chem. Rev.*, 2002, **230**, 127) and they also attract attention as nitrogen-rich energetic materials (D.E. Chavez, M.A. Hiskey and D.L. Naud, *Propellants, Explosives, Pyrotechnics*, 2004, **29**, 209).

Recent synthetic applications of the unsubstituted 1,2,4,5-tetrazine in our laboratory are illustrated by the following scheme (I.A. Gural’skiy, P.V. Solntsev, H. Krautscheid and K.V. Domasevitch, *Chem. Commun.*, 2006, 4808; K.V. Domasevitch, P.V. Solntsev, I.A. Gural’skiy, H. Krautscheid, E.B. Rusanov, A.N. Chernega, J.A.K. Howard, *Dalton Trans.*, 2007, 3893).



In fact, there are only very limited number of publications concerning chemistry of this exceptional substance, which is connected with its non-trivial synthesis and such properties as 1) instability; 2) very high volatility even at r.t.; 3) ability to explode.

As adaptation of 1,2,4,5-tetrazine preparation for basic student practicum in Kiev University, we have elaborated very simple synthetic procedure. It is a rational combination of two literature syntheses (A.T.M. Marcelis, H.C. van der Plas, *J. Heterocyclic Chem.* **1987**, *24*, 545; J. Sauer, D.K. Heldmann, J. Hetzenegger, J. Krauthan, H. Sichert, J. Schuster, *Eur. J. Org. Chem.* **1998**, 2885), which was significantly simplified in order to shorten the experiment time, to achieve excellent reproducibility and to avoid any procedures connected with column chromatography separations and inert atmosphere technique. Present procedure is optimized for two 8-hour working days.



93.6 g of solid formamidinium acetate (ACROS, 99%) was placed in a 1 L flask equipped with a mechanic stirrer, thermometer and addition funnel. The flask was placed in ice bath and 120 mL of pre-cooled (0^{o}C) hydrazine hydrate (ACROS, 64% hydrazine) was added during 10 min with stirring. The initially formed clear solution rapidly solidifies after 5-8 min, and after this the cake was left for 1 h at r.t. Then 60 mL of ice water was added and the mixture was stirred for an additional hour in an ice bath. The solid was filtered on a Büchner funnel with suction and was made as dry as possible by efficient pressing. *In spite of oxidation of this intermediate product in air, it was not necessary to use inert atmosphere technique.*

The solid was transferred into 2 L flask equipped with a mechanic stirrer, thermometer and addition funnel and dissolved in 300 mL of pre-cooled glacial acetic acid. The mixture was placed into bath (ice/water) and 31 g of solid $NaNO_2$ was added in small portions for 2 h at 0^{o}C (ice bath) and with stirring. After additional 1 h of stirring at this temperature, the ice/water bath was replaced with an efficient ice/NaCl bath and the mixture was cooled to -18^{o}C and then 450 mL of ice water was added at once [*Efficient pre-cooling is critical for the success of the synthesis, since the addition of water effects rapid and pronounced rise of temperature, after 1-2 minutes: from -18^{o}C to +15^{o}C. When, without the pre-cooling, in some*

experiments the reaction mixture temperature exceeded 30°C, the yield of the product was significantly lower].

After the exothermic effect ceased, the reaction mixture was again cooled to 0°C. The solution was extracted with 4 × 400 mL of cold CH_2Cl_2, the combined extracts were washed with 1 L of saturated $NaHCO_3$ solution and with 0.8 L water, and then dried overnight over $CaCl_2$ in a refrigerator. The red-violet solution was evaporated to a volume of 60-70 mL by distillation of the solvent from a 500 mL flask through a 60 cm Vigreux column [*the red-colored distillates were used for extractions of the next batch doing by another student*]. The residual liquid was transferred into 250 mL flask. Some solvent remained was evaporated *in vacuo* and the solid left was sublimed at r.t. and 1.0 Torr directly from the flask on a cooling finger (using a usual adapter for condensation of liquid ammonia or volatile amines – This simple apparatus was illustrated in supplementary material for publication K.V. Domasevitch, I.A. Gural'skiy, P.V. Solntsev, E.B. Rusanov, H. Krautscheid, J.A.K. Howard, A.N. Chernega. *Dalton Trans.*, 2007, 3140). The temperature of cooling finger was maintained at -40°, using acetone/liquid N_2. Sublimation yields pure product as deep-red very volatile crystals. The typical yields were 8.5-10 g. In many experiments the yield approached 15 g.

This product significantly decomposes at r.t. in air for a period of 2-3 weeks, but may be stored for an indefinitely long term in a refrigerator (-20°C).

Crystal structure determination and refinement

Crystallography

The intensity data were collected at 213 K on a Stoe Imaging Plate Diffraction System [1]: ϕ oscillation scans 0–180°, step $\Delta\phi$ = 1.0° (ϕ = 0-200°, $\Delta\phi$ = 0.7° for **2**) and on a Bruker APEX area-detector diffractometer for **3, 6** and **7** (173 K, absorption corrections by SADABS) (graphite monochromated Mo-Kα radiation, λ = 0.71073 Å). The structures were solved by direct methods and refined in the anisotropic approximation using SHELXS-97 [2] and SHELXL-97 [3]. Details are given below. Graphical representation of the crystal structures was made using program Diamond [4].

1. Stoe & Cie (2000). *IPDS Software*. Stoe & Cie GmbH, Darmstadt, Germany.
2. G.M. Sheldrick, *Acta Crystallogr.*, 1990, **A46**, 467.
3. G.M. Sheldrick, SHELXL97, A system of computer programs for X-ray structure determination, University of Göttingen, Göttingen, Germany, 1997.
4. K. Brandenburg, Diamond 2.1c, Crystal Impact GbR, Bonn, 1999.

Refinement of the structures

Structure $[Cu_2(bpph)(CH_3CN)_2\{S_2O_6\}]$ (1)

The structure was solved by direct methods. All H atoms were located from difference maps and then refined a riding, with C---H (aromatic) distances constrained to 0.94 Å, and C---H (methyl) distances constrained to 0.97 Å, with $U_{iso}(H) = 1.2U_{eq}$ (parent aromatic carbon atoms) and $U_{iso}(H) = 1.5U_{eq}$ (parent methyl cartbon atom).

The bipyridazine ligand lies across an inversion centre and the dithionate anion lies across twofold axis.

Structure $[Cu_4(bpph)_5](BF_4)_4 \cdot 4CHCl_3$ (2)

The structure was solved by direct methods. All CH (aromatic) H atoms were located from difference maps and then refined a riding, with C---H distances constrained to 0.94 Å, and with $U_{iso}(H) = 1.2U_{eq}$ (parent carbon atoms).

Both independent solvate chloroform molecules are disordered: one of them shows very typical 'rotational' disorder, while other one is disordered over two very closely separated positions. Contributions of the disorder components were refined (partial occupancy factors are 0.42/0.58 and 0.43/0.57). Atoms of these disordered chloroform molecules were left isotropic and the hydrogen atoms were not added. Standard geometry constraints (C---Cl bond lengths and Cl---C---Cl bond angles) were applied in order to improve the refinement stability.

One of the BF_4^- anions is possibly disordered, as was indicated by the relatively high values for the thermal motion. We were not successful to resolve the possible disorder. All atoms of the counter anions were refined anisotropically and without any constraints in the geometry.

One of three unique (tetradentate) bipyridazine molecule lies across an inversion centre.

Structure $[Ag(bpph)\{NO_3\}] \cdot CHCl_3$ (3)

The structure was solved by direct methods. All H atoms were located from difference maps and then refined a riding, with C---H distances (aromatic) constrained to 0.93 Å, C---H distances (chloroform) constrained to 0.98 Å, and with $U_{iso}(H) = 1.2U_{eq}$ (parent carbon atom).

Both unique bipyridazine molecules, either bidentate and tetradentate, lie across inversion centres.

Structure $[Ag_4(bpph)_3\{CF_3COO\}_4] \cdot CH_3CN$ (4)

The structure was solved by direct methods. All H atoms (aromatic CH) were located from difference maps and then refined a riding, with C---H distances constrained to 0.94 Å, and with $U_{iso}(H) = 1.2U_{eq}$ (parent carbon atom).

Both unique trifluoroacetate groups shows very typical rotational disorder. The refined partial contributions were 0.5/0.5 and 0.6/0.4. For each of the disorder contributions, the geometry of the CF_3 group was restrained (either C---F distances or F---C---F bond angles, generating in total 41 restraints), while all the disordered atoms were refined anisotropically.

The solvate acetonitrile molecule is disordered over two closely situated positions related by inversion center (0.5/0.5). The atoms were refined anisotropically and the hydrogen atoms of the methyl group were not added.

The bidentate bipyridazine ligand is situated across an inversion centre.

Structure [Ag(*bpph*){C_2F_5COO}] (5)

The structure was solved by direct methods. All H atoms were located from difference maps and then refined a riding, with C---H distances constrained to 0.94 Å, and with $U_{iso}(H) = 1.2U_{eq}$ (parent carbon atom).

Relatively high thermal values for atoms of pentafluoropropionate group indicated possible disorder. It was not possible to resolve it. The atoms were refined anisotropically for the sake of overall convergence and no geometry restraints were applied.

Both unique bipyridazine molecules, either bidentate and tetradentate, lie across inversion centres.

Structure [Ag_4(*bpph*)$_3${CH_3SO_3}$_4$]·2$CHCl_3$ (6)

The structure was solved by direct methods. All H atoms (aromatic CH) were located from difference maps, while methyl CH_3 atoms were added geometrically and then refined a riding, with C---H distances (aromatic CH) constrained to 0.94 Å, C---H distances (methyl) constrained to 0.97 Å, and with $U_{iso}(H) = 1.2U_{eq}$ (parent aromatic carbon atom) and $U_{iso}(H) = 1.5U_{eq}$ (parent methyl carbon atoms).

One of the unique methanesulfonate anions is equally disordered over two overlapping position. The disorder was resolved with a set of restraints in geometry: S---C 1.77(1) Å, S---O 1.45(1) Å and with idealized tetrahedral geometry around sulfur atom. Also, EADP constraint was applied separately to atoms of each of the disorder components. In total, 14 restraints were generated. The hydrogen atoms were not added to this disordered methanesulfonate.

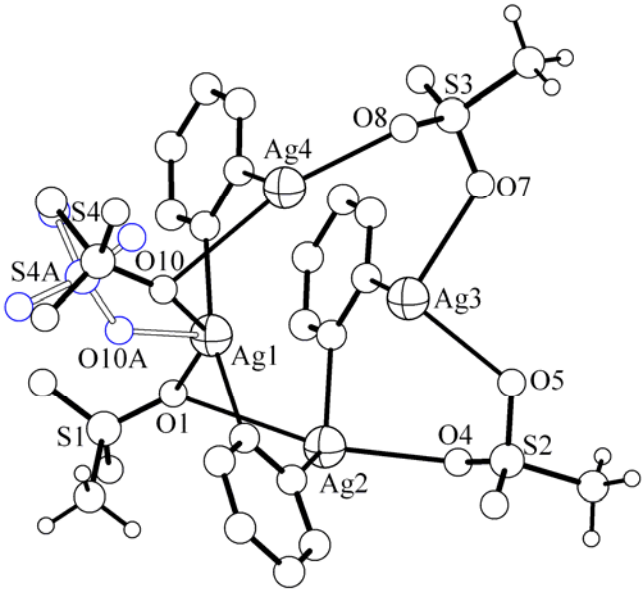


Figure S1. The refined disordering model for on of the methanesulfonate anions in structure **(6).**
(For the second contribution of the disorder, the atoms [O10A, S4A] are marked with index A)

Both solvate chloroform molecules were badly disordered and was impossible to find a resonable and refinable disordering scheme. Therefore, the remaining electron density in the structure was modelled using a SQUEEZE routine.

Structure [Ag_2(*bpph*){$C_6H_5CO_2$}$_2$]·2H_2O (7)

The structure was solved by direct methods. All H atoms were located from difference maps and then refined a riding, with C---H distances constrained to 0.93 Å, and with $U_{iso}(H) = 1.2U_{eq}$ (parent carbon atom).

For solvate water molecule, the oxygen atom was disoredred over two closely separated positions with partial occupancies 0.7 and 0.3, and with common positions of hydrogen atoms for two components. These hydrogen atoms were located from the map and then their positions were fixed, with $U_{iso}(H) = 1.5U_{eq}$ of the parent oxygen atom (which was a predominant 0.7 component of the disorder).

The pyridazine ligands and disilver/pyridazine dimers are situated across inversion centres.

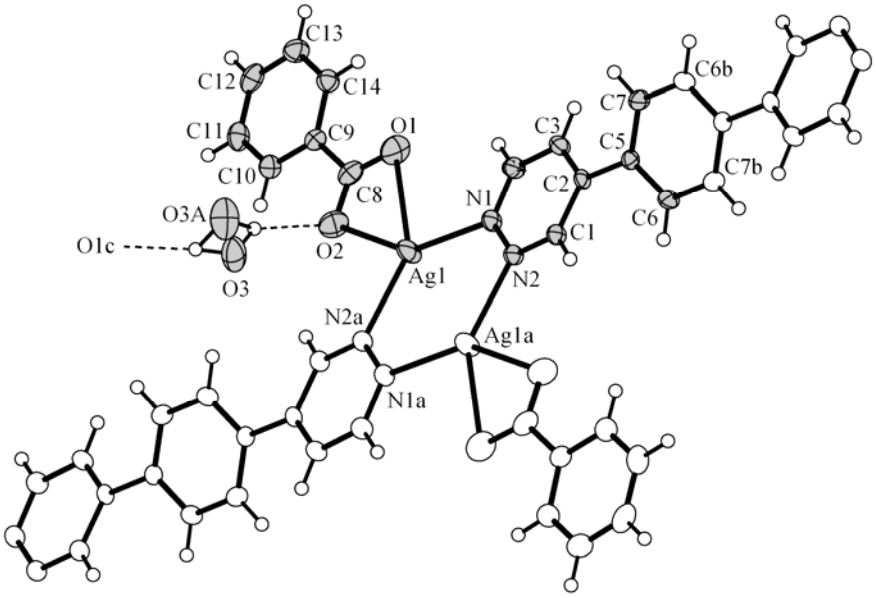


Figure S2. Atom labeling scheme for structure **(7)**. Thermal ellipsoids are drawn at 40% probability level and the unique part of the structure is marked grey. Note mode of the disorder for hydrogen-bonded water molecule (O3/O3A).
[Symmetry codes: (a) –x, -y, 1-z; (b) -1-x, -y, 2-z; (c) x, 0.5-y, -0.5+z]

Structure $[Ag_6(bpph)_3(H_2O)_6\{C_6H_4(CO_2)_2\}_2]C_6H_4(CO_2)_2 \cdot 4H_2O$ (8)

The structure was solved by direct methods. All H atoms for the pyridazine ligand, coordinated isophthalate anion and three coordinated water molecules were located from difference maps and then refined as riding (for water molecules the hydrogen atoms were fixed), with C---H distances constrained to 0.94 Å, and with $U_{iso}(H) = 1.2U_{eq}$ (parent carbon atom) and $U_{iso}(H) = 1.5U_{eq}$ (parent oxygen atoms).

One of two unique bipyridazine ligands is situated across an inversion centre.

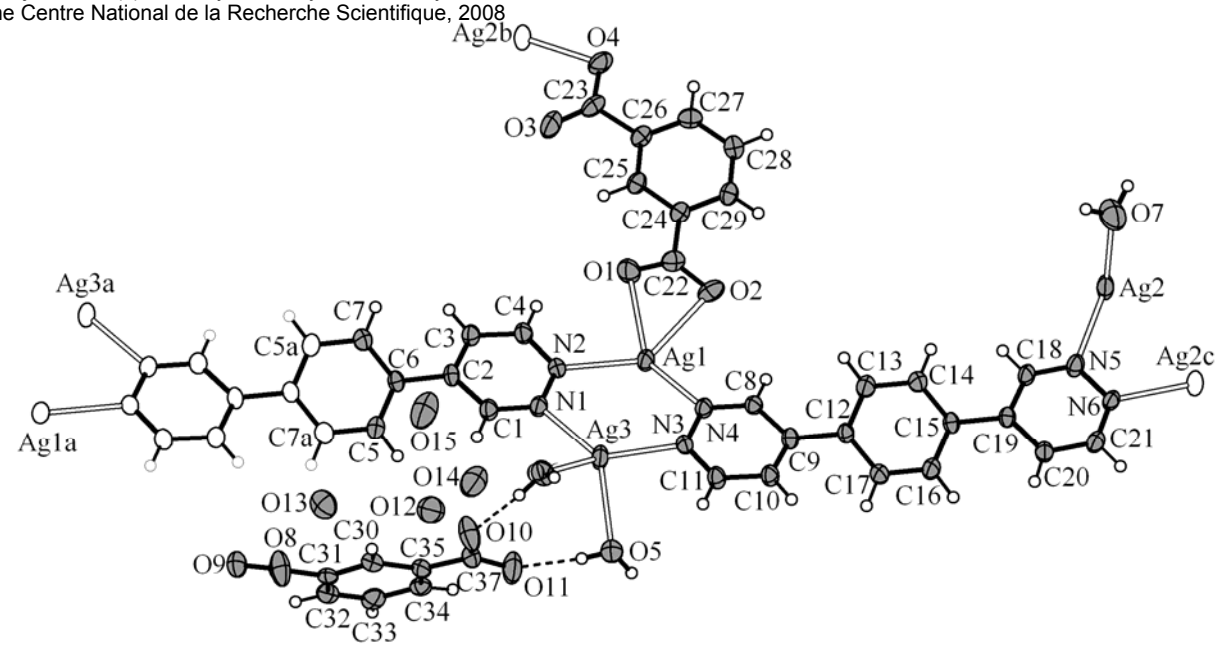


Figure S3. Atom labeling scheme for structure **(8)**. Thermal ellipsoids are drawn at 40% probability level and the unique part of the structure is marked grey. Note the disposition of non-coordinated isophthalate anion, which is hydrogen-bonded to pair of the coordinated aqua-ligands.
[Symmetry codes: (a) 2-x, 1-y, 2-z; (b) 2-x, -y, -z; (c) –x, -1-y, -1-z]

The non-coordinated isophthalate anion was disordered by the symmetry, and in such a manner that carbon-2 atom of the carbocycle occupies a center of inversion and it is common for both the disorder components. The carboxyl groups from both components were overlapped with very short interatomic separations and therefore some minor restraints were applied in order to improve the refinement stability. In particular, planarity of both C-CO_2 fragments was imposed with FLAT restraints and with distance C---C fixed at 1.480(5) Å. For carboxylic atoms of two disorder components the corresponding C---C distance was about 0.16 Å and therefore EADP restraint was applied to thermal parameters of these two atoms. However, it was possible to refine all disordered atoms anisotropically, and the hydrogen atoms were added geometrically, with partial contribution factors 0.5.

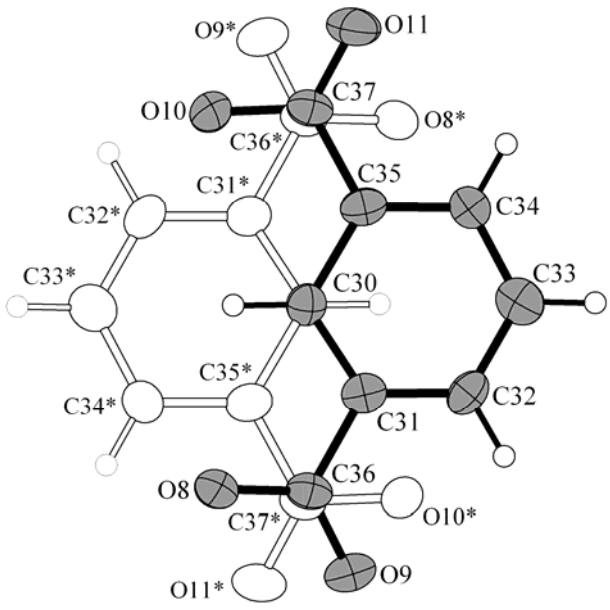


Figure S4. The refined disordering scheme for the non-coordinated isophthalate dianion in structure **(8)**. Two components of the disorder (grey and white, which are marked by an asterisk) are related by inversion [**symmetry code**: (*) 1-*x*, 1-*y*, 2-*z*] in such a way that atom C30 resides on a inversion centre and it is a common atom for both contributions. Other atoms of the disordered moiety were refined with partial occupancy factors 0.5.

Two unique solvate water molecules are hydrogen bonded to the disordered isophthalate anion and therefore they are also disordered over two equal positions (0.5/0.5), depending on the orientation of the isophthalate. Both contributions were refined isotropically, and hydrogen atoms were not added to these water molecules.