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First organic-inorganic hybrid material based on $AgNO_3$ and 3-pyridine containing 2-thiohydantoin

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The reaction of 2-(methylthio)-3-phenyl-5-(pyridine-3-ylmethylene)-3,5-dihydro-4*H*-imidazol-4-one (L) with $AgNO_3$ in MeCN–CH_2Cl_2 results in the formation of coordination polymer framework. Single crystal X-ray study of the product reveals the presence of non-interpenetrating 2D nets possessing a rare topology.

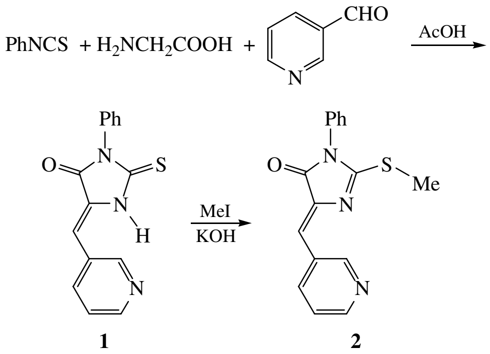
Coordination polymers, including those in which extended inorganic metal–ligand networks are linked by *exo*-polydentate organic ligands (so-called organic-inorganic hybrid materials), received considerable attention due to their potential use as catalytic, luminescent, magnetic and non-linear optic materials.[1] Multidimensional networks based on metal centres linked by rigid bridging components such as 4,4′-bipyridine are well known.[2,3] Less attention has been paid to the use of flexible bridging units in the construction of extended networks, but this approach looks quite attractive because the flexibility and conformation freedoms of such ligands might offer the possibility for the formation of unprecedented frameworks with tailored properties and functions. Recently, some representative examples of the Ag^I coordination compounds based on N,S-containing flexible ligands have been reported.[4,5]

2-Thiohydantoins substituted at the C-5 position exhibit a wide range of pharmacological activities including antiviral, antitumor and antimycobacterial ones. They present the important structural features of several aldose reductase inhibitors.[6,7] Given this level of biological activity, the synthesis of coordination compounds, which incorporate the thiohydantoin fragment, could have significant impact in the field of drug design and drug delivery. 2-Thiohydantoins are known as ligands capable of coordinating Hg^{II} or Tl^{III} ions *via* nitrogen and/or sulfur donor atoms;[8] they can also form supramolecular networks by hydrogen bonds like NH···S and NH···O.[9]

In this paper, the synthesis of heterotopic multidentate ligand 2-(methylthio)-3-phenyl-5-[(*Z*)-pyridin-3-ylmethylene]-3,5-dihydro-4*H*-imidazol-4-one **2** is described. We also began to study the complexation ability of the ligand towards transition and main group metals. Here, we report the synthesis and crystal structure of the coordination compound $[(AgL)_2(NO_3)_2]_n$ (where L = **2**).

Compound **1** was prepared by three-component condensation from phenyl isothiocyanate, glycine and 3-pyridine carboxaldehyde (Scheme 1). Ligand **2** was obtained by the alkylation of **1** with methyl iodide in basic media.‡

Ligand **2** possesses three potential donating sites, namely, thioether-type bivalent sulfur atom, imine nitrogen atom from the pyridine ring and imine nitrogen atom from the thiohydantoin ring. Previously,[10] it was shown that, in the case of the ligand with a 2-pyridine fragment, a chelate complex was obtained in the reaction with cobalt chloride.



Scheme 1

The reaction of **2** with $AgNO_3$ in the acetonitrile/dichloromethane system leads readily to product **3** (Scheme 2)§. A single crystal X-ray study of **3** reveals that the complex is polymeric, and complexation occurs *via* sulfur and pyridine nitrogen.¶

In crystals of **3**, each silver atom has distorted tetrahedral coordination arrangements being linked to sulfur atom from one ligand, pyridine nitrogen atom from another ligand and two oxygens from distinct nitrates. Additional weak interac-

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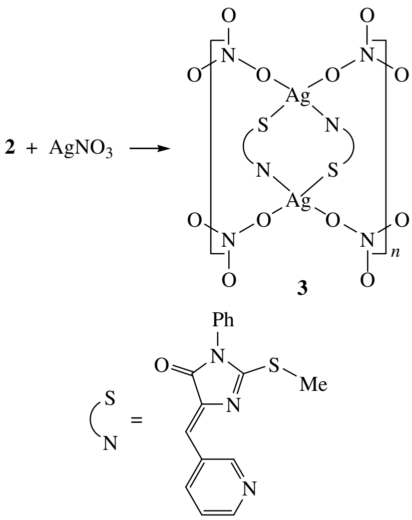
‡ For **1**: to a mixture of phenyl isothiocyanate (1.62 g, 12 mmol), glycine (0.75 g, 10 mmol) and pyridine carboxaldehyde (1.07 g, 10 mmol) 15 ml of glacial acetic acid was added. The mixture was heated for 4 h under reflux. The precipitate formed was filtered off and recrystallised from acetic acid. Yield, 1.64 g (61%); mp 216 °C. ^{1}H NMR ([$^2H_6$]DMSO) δ: 12.45 (br. s, 1H, NH), 8.94 (d, 1H, H_α-Py, *J* 18.8 Hz), 8.51 (d, 1H, $H_{\alpha'}$-Py, *J* 8.3 Hz), 8.25 (d, 1H, H_γ-Py, *J* 8.3 Hz), 7.42 (m, 6H, $H_{\beta'}$-Py, H-Ph), 6.71 (s, 1H, =CH). IR (KBr, ν/cm^{-1}): 3260 (NH), 1730 (C=O). Found (%): C, 63.93; H, 3.72; N, 14.65. Calc. for $C_{15}H_{11}OSN_3$ (%): C, 64.06; H, 3.91; N, 14.95.

For **2**: 3-phenyl-5-[(*Z*)-3-pyridinemethylidene]-2-thiohydantoin (10 mmol) was suspended in ethanol (5 ml) and water (5 ml). To this mixture 0.5 ml of a 15% aqueous solution of KOH was added, followed by 20 mmol of MeI. After stirring for 15 min at room temperature, the precipitate was filtered off. Yield, 71%; mp 167 °C (EtOH). ^{1}H NMR ([$^2H_6$]DMSO) δ: 9.22 (s, 1H, H_α-Py), 8.69 (d, 1H, $H_{\alpha'}$-Py, *J* 8.3 Hz), 8.53 (d, 1H, H_γ-Py, *J* 4.4 Hz), 7.46 (m, 6H, $H_{\beta'}$-Py, Ph), 6.88 (s, 1H, CH=), 2.70 (s, 3H, Me). IR (KBr, ν/cm^{-1}): 1730 (C=O), 1650 (C=N), 1600 (C=C). Found (%): C, 65.22; H, 4.09; N, 14.25. Calc. for $C_{16}H_{13}OSN_3$ (%): C, 65.00; H, 4.41; N, 14.24.

§ For **3**: the solution of 10 mg (0.034 mmol) of **2** in 3 ml of methylene chloride was slowly diffused over 3 ml of an acetonitrile solution containing 6 mg (0.034 mmol) of $AgNO_3$. After two days, yellow crystals suitable for X-ray analysis were obtained.



Scheme 2

tion between Ag(1) and O(1) atoms of nitrate groups with an interatomic distance of 2.76 Å should be regarded as secondary interaction. Two formula units are linked together by opposite ends of ligands in a head-to-tail orientation thus forming a 18-membered metallamacrocycle (Scheme 2). The picture of two neighbouring $(C_{16}H_{13}AgN_4O_4S)_2$ dimers is shown in Figure 1. The distances between silver atoms within the dimers are 10.51 Å.

The heteroaromatic cycles of the ligands are almost parallel to each other with dihedral angles between them not exceeding 10°. The distance between N(11) and H(3) (2.47 Å) points to weak intramolecular hydrogen bonding. Both pyridine and thiohydantoin rings are almost in-plane, the dihedral angle between respective mean planes equals to 8.5°. The shortest carbon–carbon contact within the dimers is C(3)···C(3) 3.22 Å, which indicates[13] a strong π–π interaction between adjacent ligands. We believe that this interaction is a result of coordination of sulfur to silver, which brings the linked molecules to such a close distance.

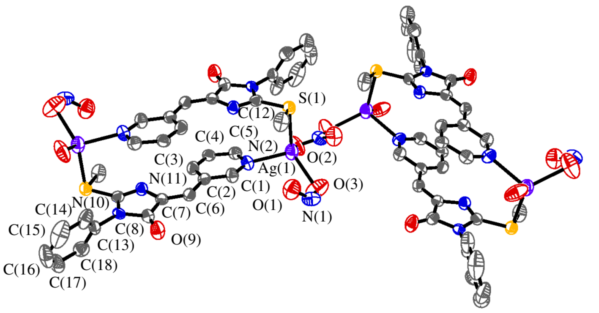


Figure 1 ORTEP representations of **3** showing atom numbering scheme (hydrogen atoms are omitted for clarity, the thermal ellipsoids representing 50% probability). Selected bond lengths (Å) and angles (°): Ag(1)–S(1) 2.601(4); Ag(1)–N(2) 2.317(10); Ag(1)–O(2) 2.462(12); Ag(1)–O(3) 2.309(12); S(1)–Ag(1)–N(2) 104.3(3); O(2)–Ag(1)–O(3) 108.9(4); N(2)–Ag(1)–O(2) 88.6(4); N(2)–Ag(1)–O(3) 112.9(4); S(1)–Ag(1)–O(2) 117.3(2); S(1)–Ag(1)–O(3) 121.5(4); Ag(1)–S(1)–C(12) 93.9(4).

Benzene rings are placed in the channels formed by six silver atoms from four dimers. The dihedral angles of both skeleton rings with the benzene ring are equal to 60.8(5)° and 68.9(5)°, respectively. It should be mentioned that some atoms of this ring have abnormally high atomic displacement parameters (ADP), rapidly increasing from C(13) to C(15) and C(16). The orientation of thermal ellipsoids shows the partial rotation around the axis through C(13) and perpendicular to the ring plane and partial incline of C(14)–C(16) aside from H(14). Due to the positioning of benzene rings in the channel their exact position in each particular unit cell may vary within a certain range of angles.

Nitrate anions act as μ-bridging bis(monodentate) ligands in between silver atoms. This linking results in the formation of infinite zig-zag chains of alternating anions and cations arranged along the crystallographic axis *c* [Figure 2(*a*)]. The shortest Ag–Ag separation within these chains is 5.71 Å. Apparently, the bridging nitrates bring together $[Ag_2L_2]$ dimers to form double layers, which lie in *bc* crystallographic plane

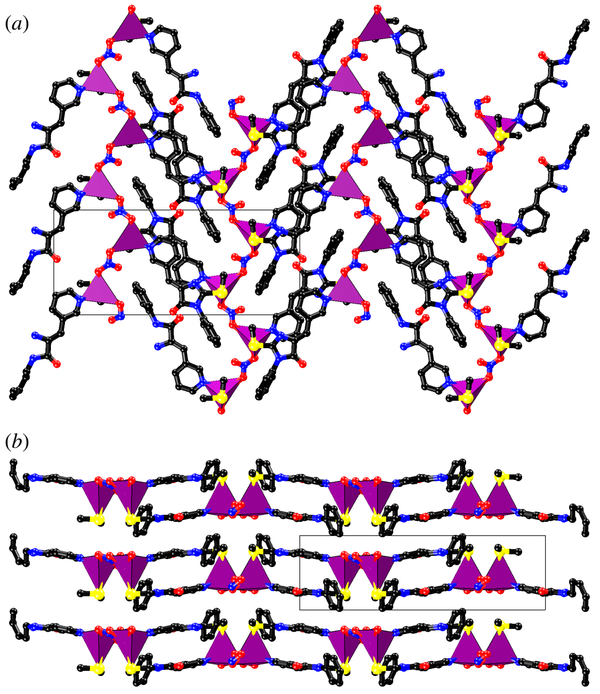


Figure 2 Crystal packing of **3**, mutual arrangements of silver coordination tetrahedra are shown. (*a*) Front view of the 2D double layers (projection along the crystallographic axis *a*, hydrogen atoms are omitted for clarity). (*b*) Back view of 2D double layers (projection along the crystallographic axis *c*, hydrogen atoms are omitted for clarity).

¶ *Crystallographic data for* **3**: crystals $C_{16}H_{13}N_4O_4SAg$, yellow prisms, crystal size, 0.42×0.19×0.15 mm, are monoclinic, space group $P2_1/c$; $a = 7.3026(13)$, $b = 23.289(3)$ and $c = 10.2812(24)$ Å; $V = 1688.9(6)$ Å^3, $Z = 4$, $d_{calc} = 1.829$ g cm^{-3}. Data were measured on a Syntex P21 diffractometer [293 K, graphite monochromator, λ(MoKα) = 0.71073 Å, ω-scan with 0.3° step]. The structure was solved by direct methods, all non-hydrogen atoms were found in turn by Fourier and difference Fourier synthesis, then refined by full matrix least squares in isotropic and anisotropic approximations. The refinement converged with $R = 0.074$. Difference Fourier synthesis revealed residual peaks at positions corresponding to hydrogen atoms. Coordinates of all possible hydrogen [except for C(20)] sites were calculated and refined with distance restrictions and fixed isotropic displacement parameters, which reduced R down to 0.069. 8452 reflections, of which 6239 were unique; 2438 of these were included in the refinement; data corrected for Lorentz and polarization effects; solution by direct methods[11,12] and refinement on $|F|$ by full-matrix least-squares procedures;[12] 263 parameters; non-hydrogen atoms were refined in an anisotropic approximation. H atoms were included, and refined in an isotropic approximation with a fixed common atomic displacement parameter; $R = 0.069$, $R_w = 0.139$.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 251159. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2007.

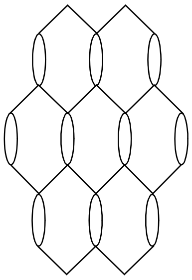


Figure 3 Network topology found in crystals of **3**.

[Figure 2(*a*)]. Two adjacent dimers in a layer are not connected to each other directly but are linked through nitrate–silver–nitrate chains thus forming centrosymmetric 34-membered metallamacrocycles [Ag–ONO–Ag–$(L)_2$–Ag–ONO–Ag–ONO–Ag–$(L)_2$–Ag–ONO] [Figure 2(*a*)]. The topology of 2D layers (Figure 3) is similar to that of single 2D net in the crystal structure of $Zn(bix)_2(NO_3)_2 \cdot 4.5H_2O$ [bix = bis(imidazole)xylene].[14]

In contrast to the literature analogue, in crystals of **3** 2D nets do not interpenetrate but rather form distinct facially interacted stacks. Double layers stack along *a** reciprocal axis (parallel to *bc* crystallographic plane) [Figure 2(*b*)]. Interlayer distances are rather large, the shortest ones are C(17)–O(3) (3.26 Å, benzene ring–nitrate group) and C(5)–N(11) (3.54 Å, pyridine ring–thiohydantoin ring). Thus, only weak interlayer bonding may be suggested. This fact is confirmed by coherent twinning in an almost 1:1 ratio resulting from opposite layer orientation within one crystal.

In conclusion, the ability of heterotritopic ligand **2** to form infinite coordination frameworks with silver nitrate inorganic counterparts was demonstrated. In the resulting product, a ligand exploits two of its donating sites, *i.e.*, the thioether sulfur atom and the imine pyridine nitrogen atom. Two ligands coordinate two metal centres in a head-to-tail manner so as to form 18-membered metallamacrocycles. These units are further connected to each other by bridging nitrate anions with final formation of 2D double layers. The topology of the 2D layers is a rare case of 2D network topologies found in the literature.

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