

Electronic Supporting Information

for

An Excursion into the Intriguing World of Polymeric Tl(I) and Ag(I) Cyanoximates

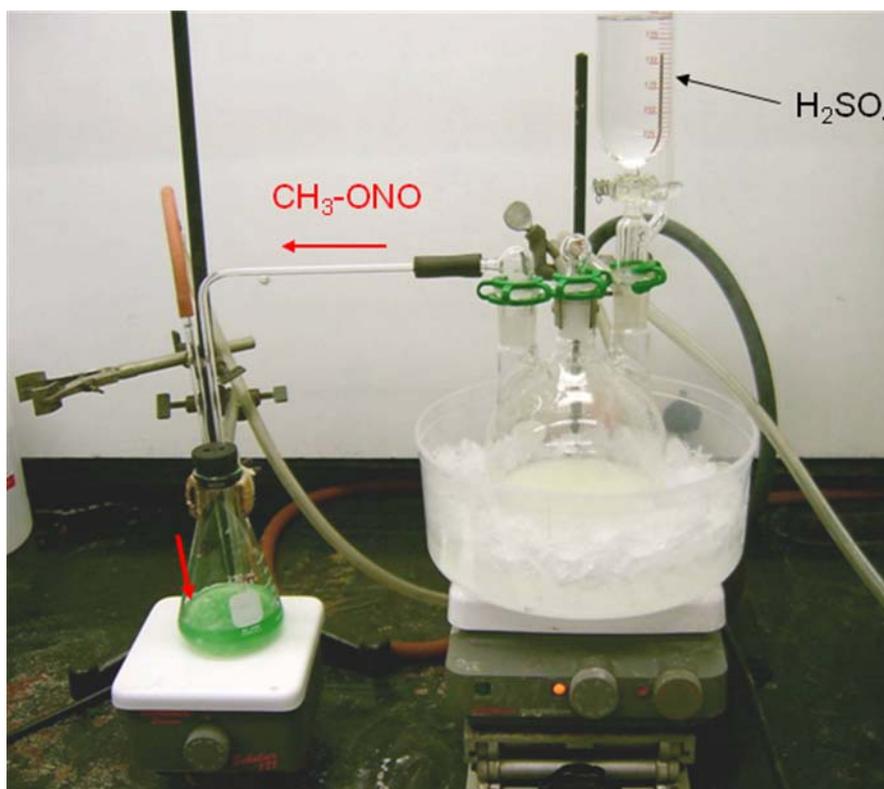
by

Nikolay Gerasimchuk

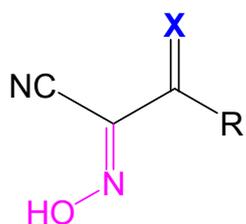
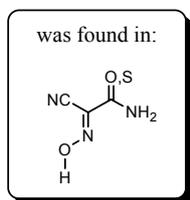
Electronic Supporting Information

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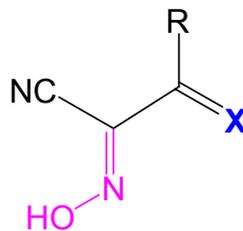
Synthesis of cyanoximes: experimental setup for the preparation of methylnitrite in route 3 on Figure 2 of the main text.



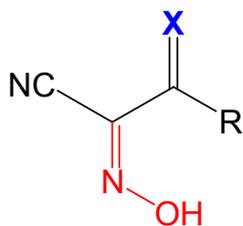
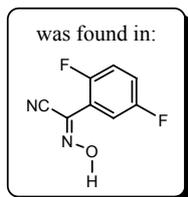
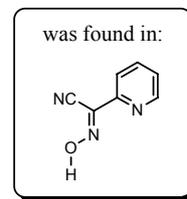
Geometrical isomerism of cyanoximes: crystallographically confirmed examples.



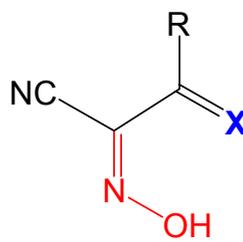
trans- anti



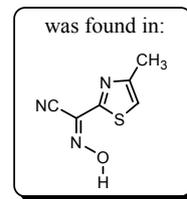
cis- anti



trans- syn



cis- syn



Values of enthalpies of bond formation, kJ/mol, for silver(I) and thallium(I) halides. (data from <http://webelements.com/>, reference 22 in the main text).

AgF	354.1	TlF	445.2
AgCl	341.4	TlCl	372.8
AgBr	293.6	TlBr	333.9
AgI	234.1	TlI	272.7

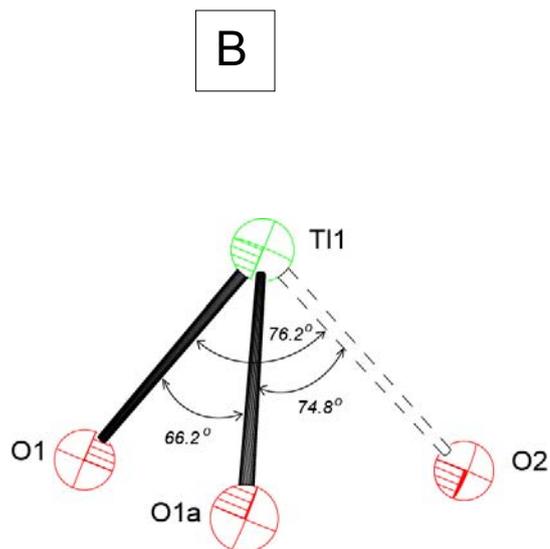
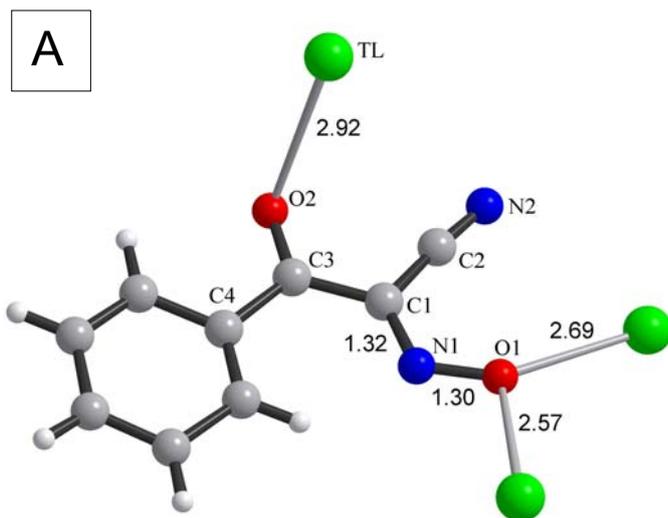
Large Dewar flask of 5 L capacity and a digital thermostat used for the crystal growth of monovalent thallium and silver cyanoximates from hot aqueous and non-aqueous solutions.



Actual photographs of some Tl-cyanoximates under the microscope - Tl(2Cl-PhCO), on the left, and Tl(4PCO) sample on the right.

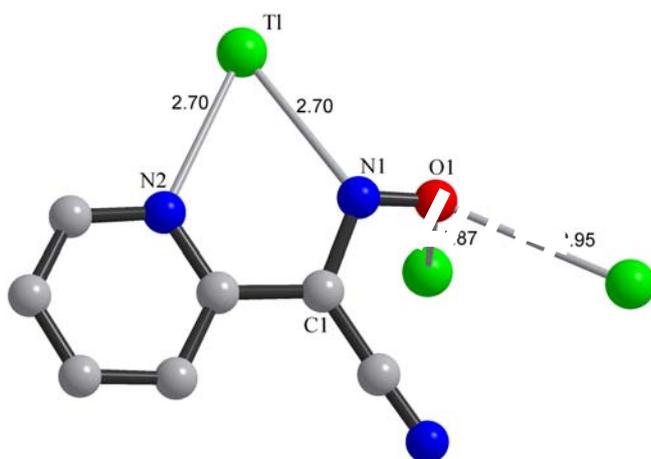


One benzoylcyanoxime (BCO⁻) anion and its cationic surrounding in Tl(BCO) complex (**A**), and structure of coordination polyhedron of the central atom (**B**). The coloring scheme here in other figures below for Tl-complexes is the following: green – Tl, red – O, blue – N, white – H.

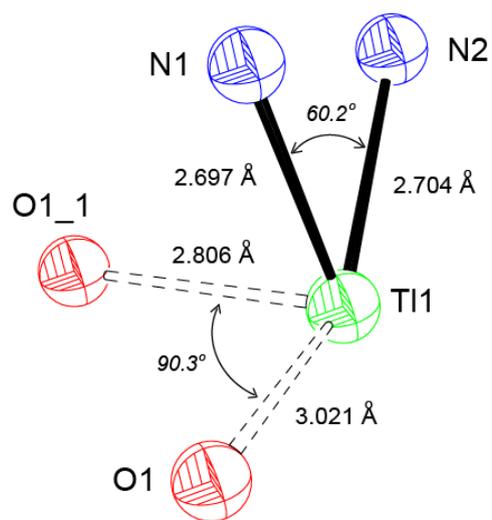


One 2-pyridylecyanoxime (2PCO) anion and its cationic surrounding in Tl(2PCO) complex (**A**), and the structure of coordination polyhedron of the central atom (**B**). Hydrogen atoms are not shown for clarity.

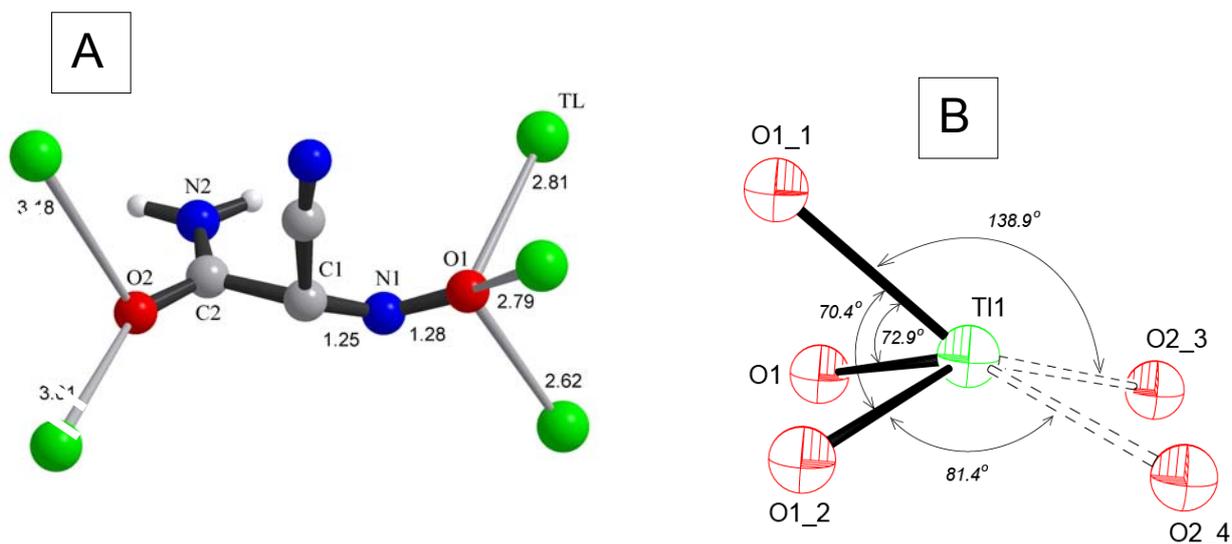
A



B



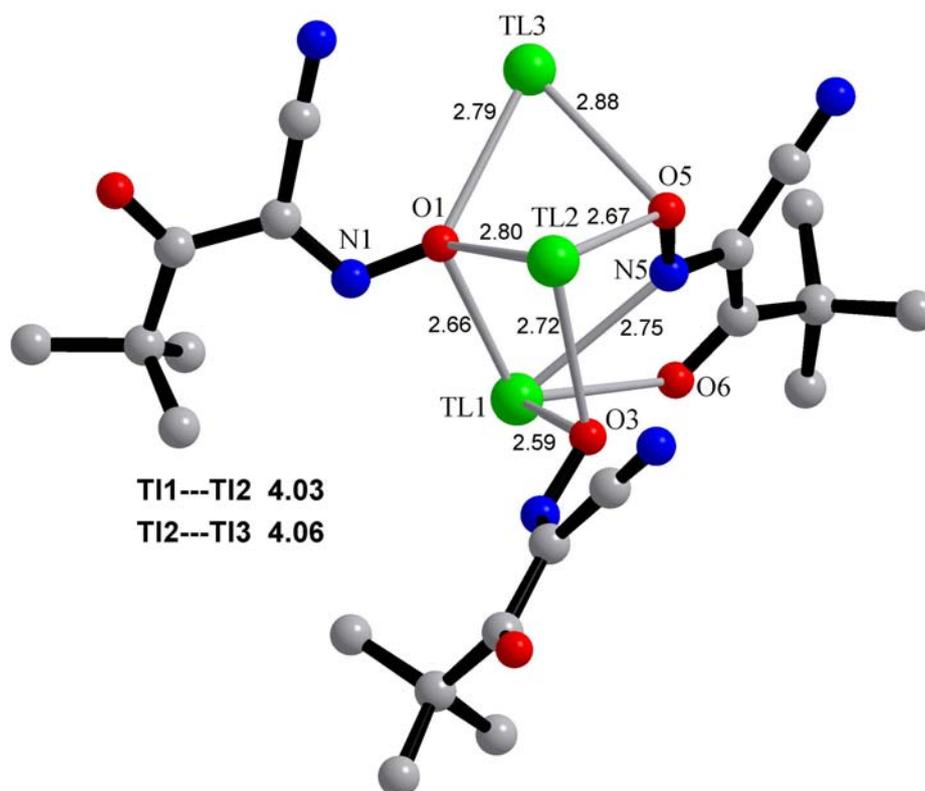
One amidecyanoxime (ACO⁻) anion and its cationic surrounding in Tl(ACO) complex (**A**), and structure of coordination polyhedron of the central atom (**B**).



Symmetry codes: #1 is $-x, -y, 3/2+z$; #2 is $1+x, 2+y, 1+z$; #3 is $3/2+x, 1/2-y, 2+z$; #4 is $3/2+x, 1/2-y, 1+z$.

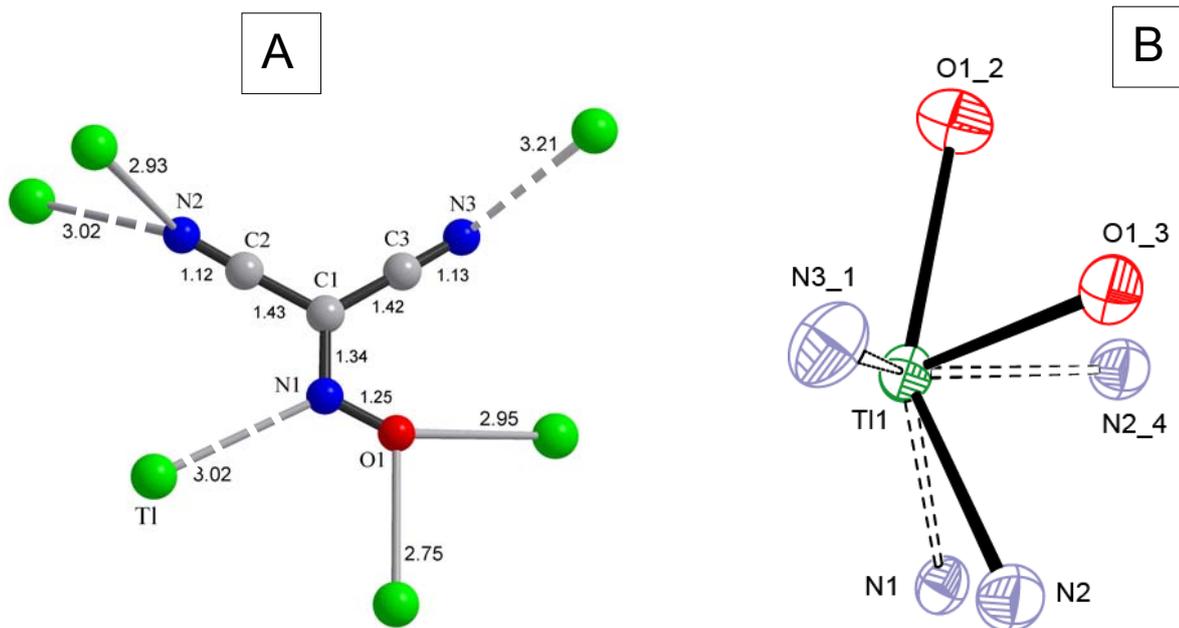
Thallium atom in this setting is at $1+x, 2+y, 2+z$.

A unique crystal structure of Tl(PiCO) showing three chemically different pyvaloil-cyanoxime anions that act as a chelate and differently bridging ligands, and three Tl(I) central atoms in different surrounding. H-atoms are omitted for clarity.

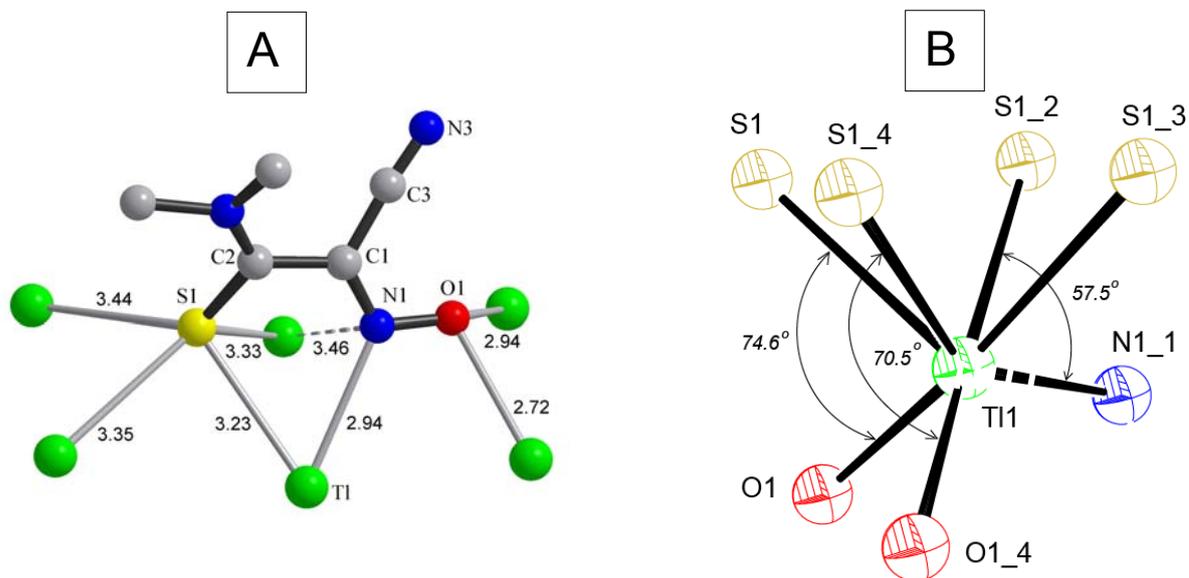


One nitrosodicyanomethanide (CCO^-) anion and its cationic surrounding in $\text{Tl}(\text{CCO})$ complex (**A**), and the structure of coordination polyhedron of the central atom (**B**). The lone pair occupies an open cleft off $\text{O1}_3 - \text{Tl1} - \text{N3}_1$ plane to the right.

Symmetry operations are: #1, x,y,z ; #2, $-x,y,-z+1/2$; #3, $-x,-y,-z$; #4, $x,-y, z+1/2$.

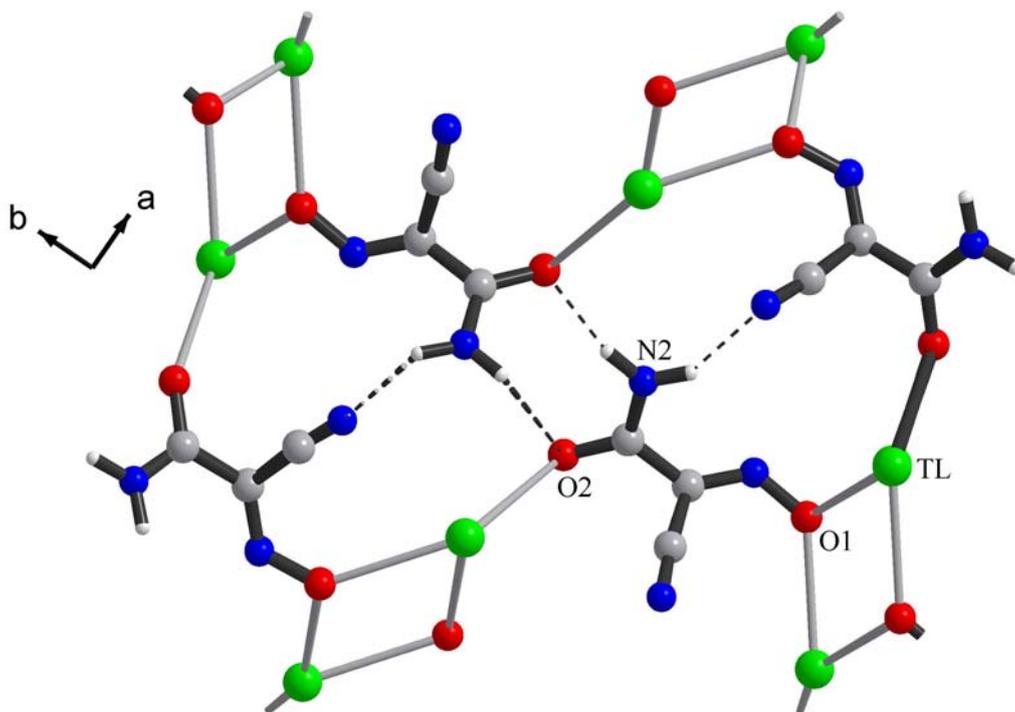


One N,N-dimethylthio-amidecyanoxime (TDCO⁻) anion and its cationic surrounding in Tl(TDCO) complex (A), and the structure of coordination polyhedron of the central atom (B).

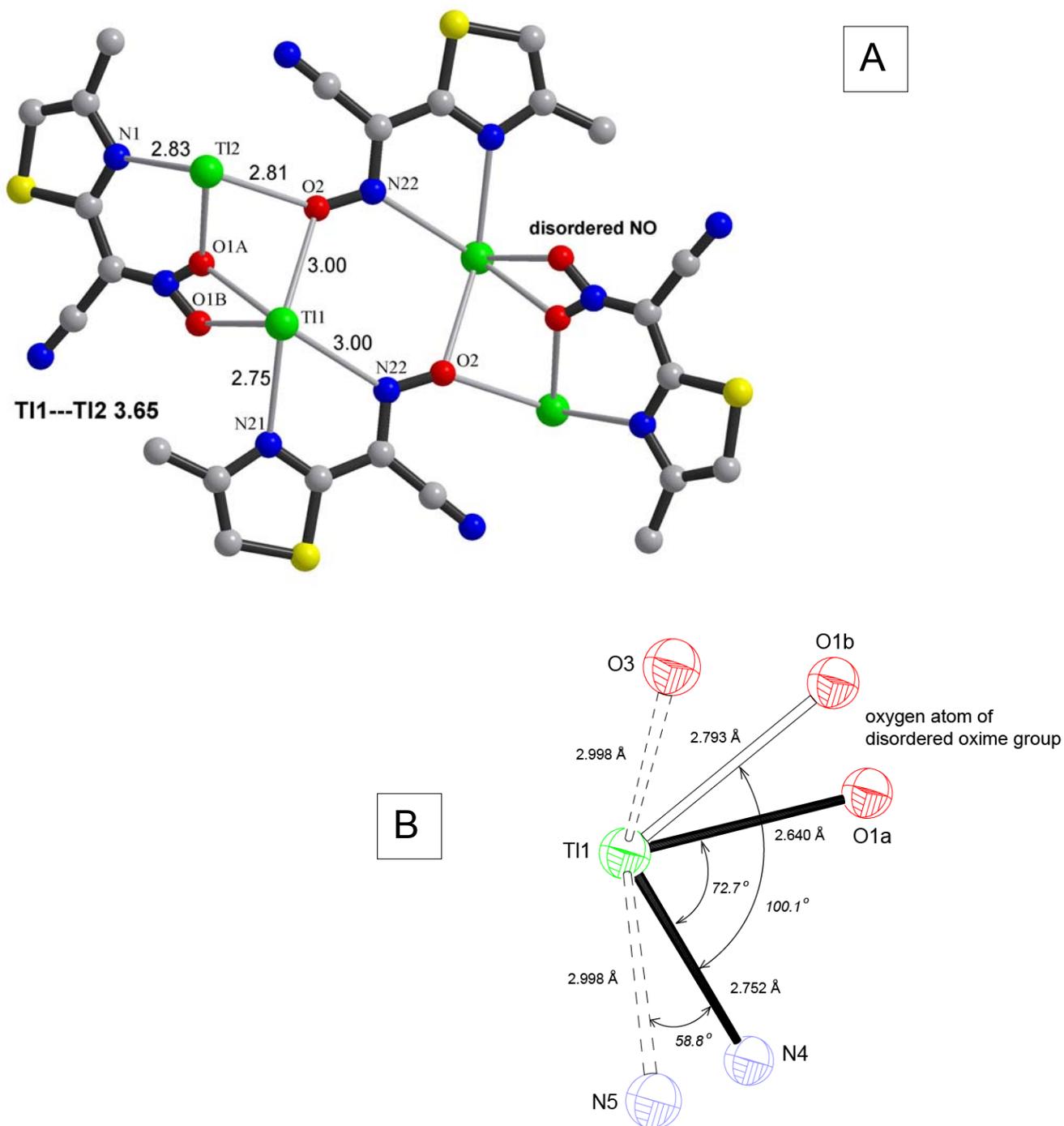


Symmetry operations: #1 x, y, z ; #2 $-x, -y, z$; #3 $x+1/2, -y+1/2, -z$; #4 $-x+1/2, y+1/2, -z$

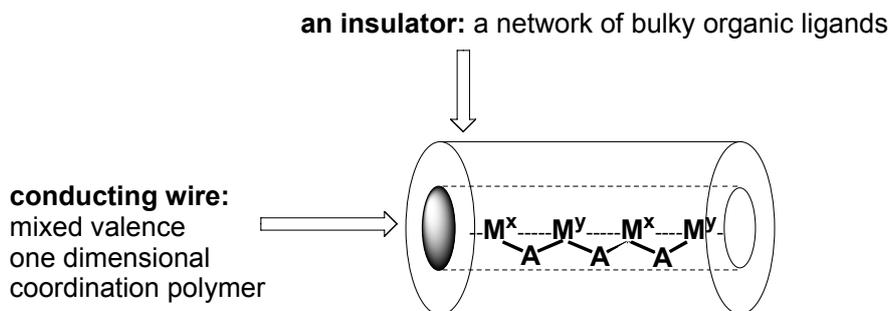
Fragment of the crystal structure of Tl(ACO) showing the formation of H-bonds that join double stranded ladder-type polymeric sheets into carcass.



Crystal structure of Tl(TLCO), which is a tetramer, containing disordered by two positions (*syn*- and *anti*- geometrical isomers) nitroso-group (A), and geometry of coordination polymer (B).

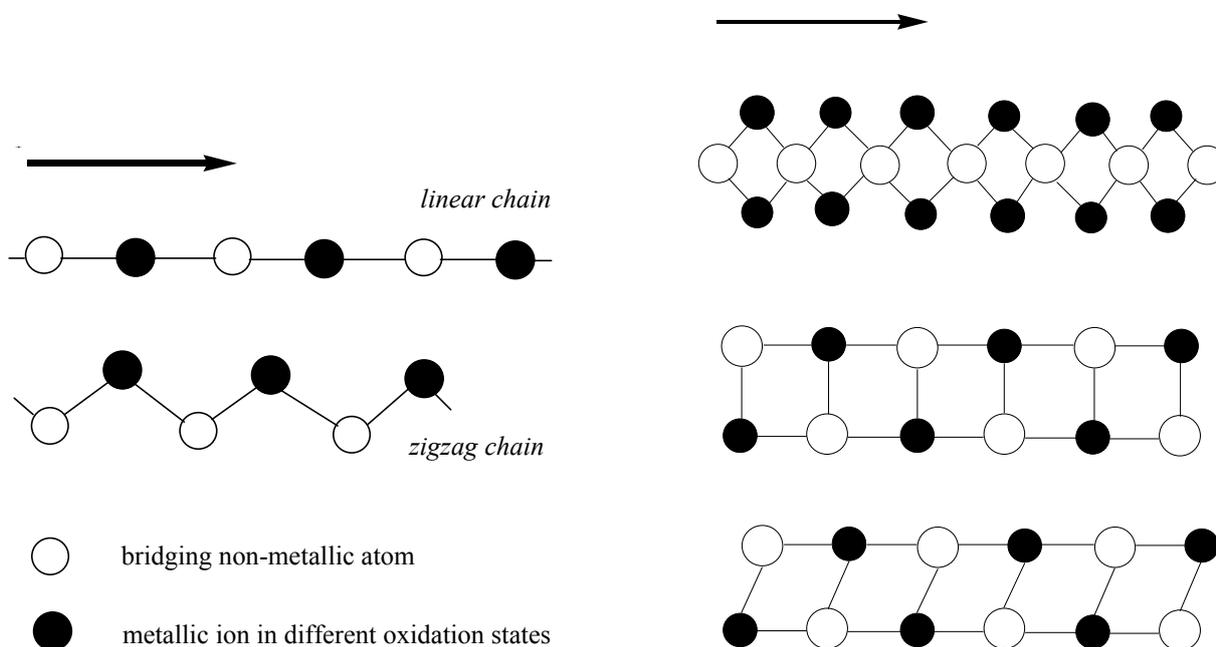


A concept of 1D-solid based on coordination polymer that consists of isolated columns of the compound with mixed valence system inside that exhibits electronic “hopping” between different oxidation states:

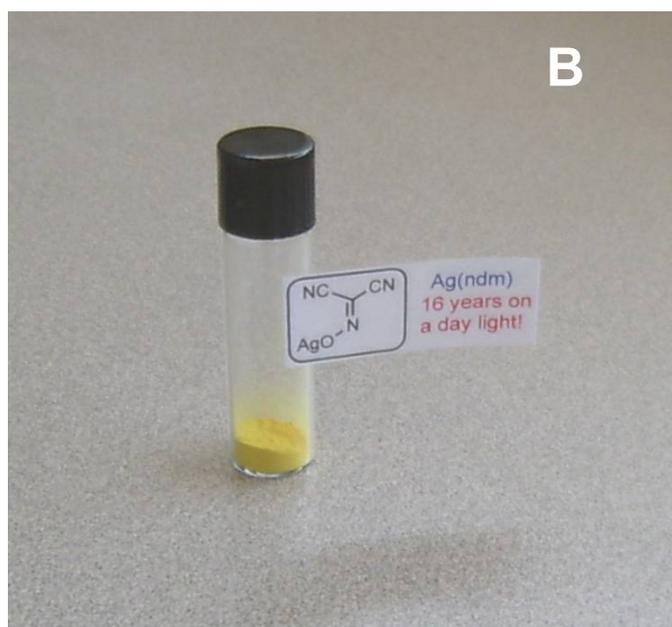


M^x and M^y are metal centers in different positive oxidation states;
 A - one or two bridging atoms, or conjugated group

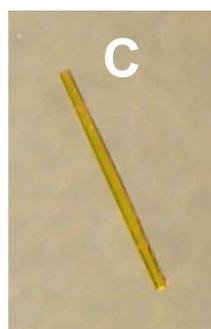
Types of 1D-coordination polymers based on the chain structure and on sheets of different arrangement. The M_2A_2 rhombs (M = metal able to have mixed valence; A = bridging donor atom) are key building blocks in these extended structures.



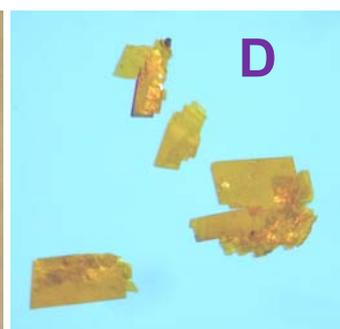
Actual photographs of light-stable Ag(I) cyanoximates in glass vials indicating the time of exposure to direct sun light (A, B), and photographs at x40 magnification of crystals of complexes used for the structure determination (C,D).



Ag(CCO)



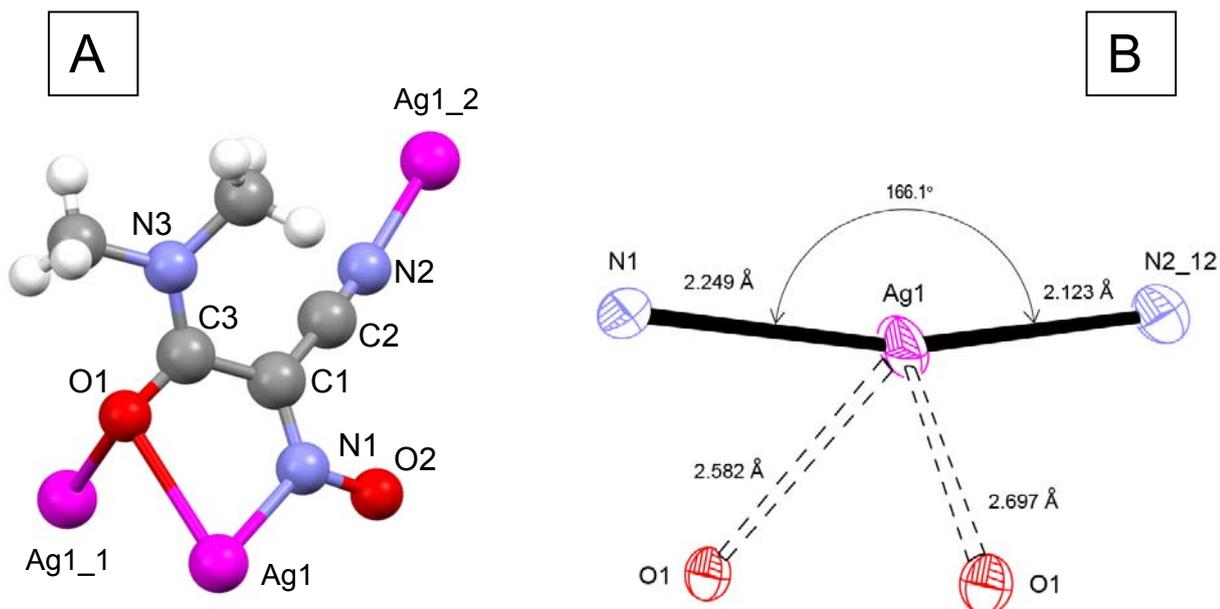
Ag(DCO)



Ag(ECO)

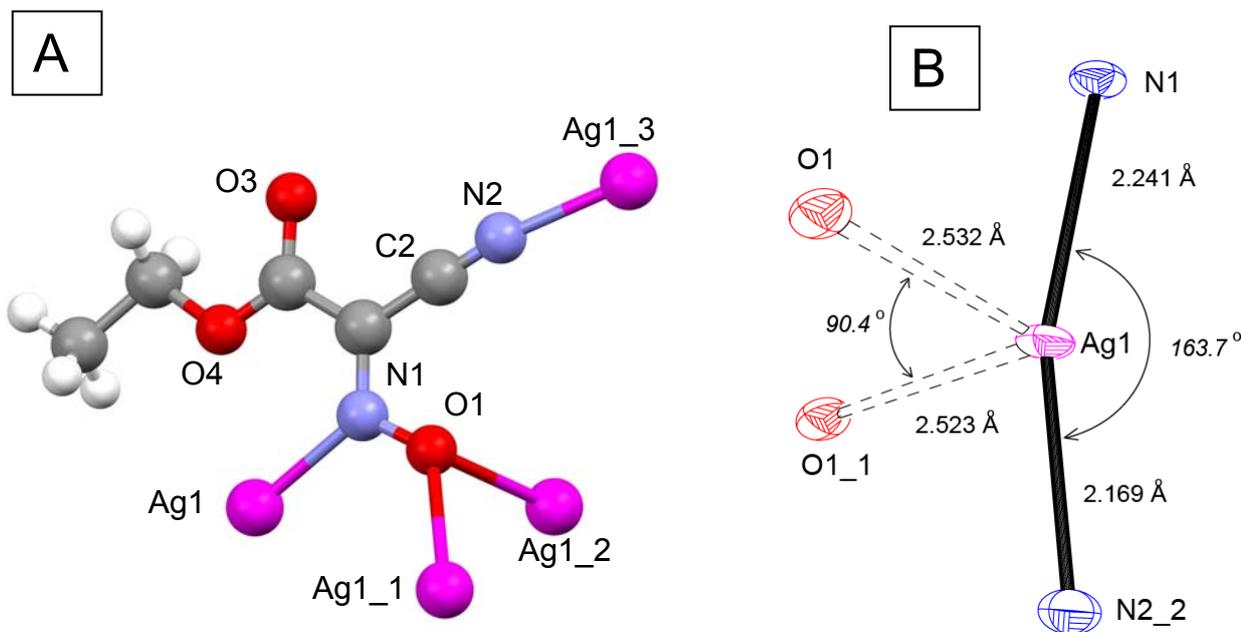
Details of geometry of the building block in the structure of Ag(DCO) complex: anion and its closest Ag⁺ surrounding (A), and geometry of coordination polyhedron in this complex (B).

Symmetry codes for silver atoms in A: for #1 $x, y, -1+z$; for #2 $-1/4+x, 3/4-y, 3/4+z$.



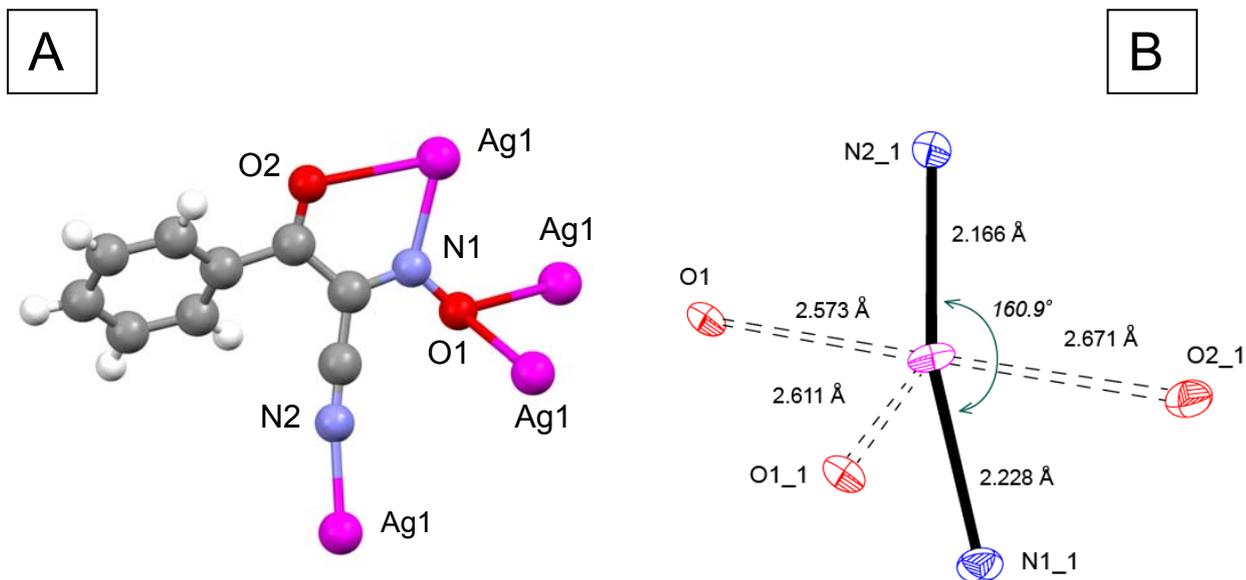
Details of geometry of the building block in the structure of Ag(ECO) complex: anion and its closest Ag⁺ surrounding (A), and geometry of coordination polyhedron in the complex (B).

Symmetry codes for silver atoms in A: for #1 -x,2-y,1-z; for #2 1-x, 2-y, 1-z; for #3 1+x, 1+y,z



The ethoxy-group OC₂H₅ in the ligand is disordered by 2 positions related by the mirror plane C1-C3. The occupancy factor is ~50% for both components. Drawn here and in the paper figures of crystal structure of Ag(ECO) contain only one domain for clarity purposes.

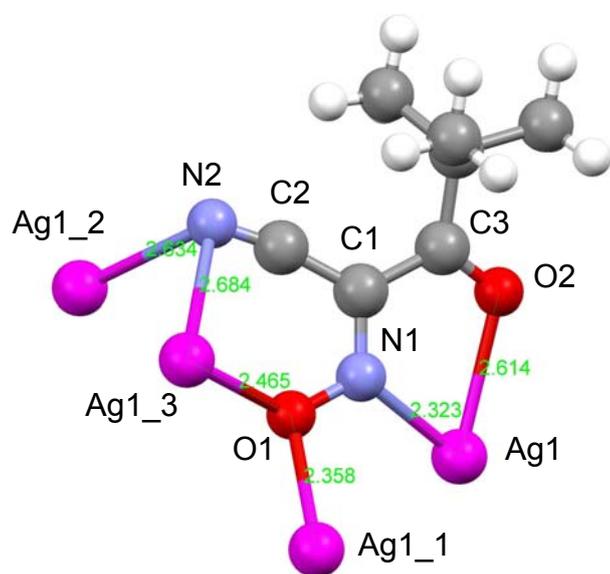
Details of geometry of the building block in the structure of Ag(BCO) complex: anion and its closest Ag⁺ surrounding (A), and geometry of coordination polyhedron of silver(I) atom in the complex (B).



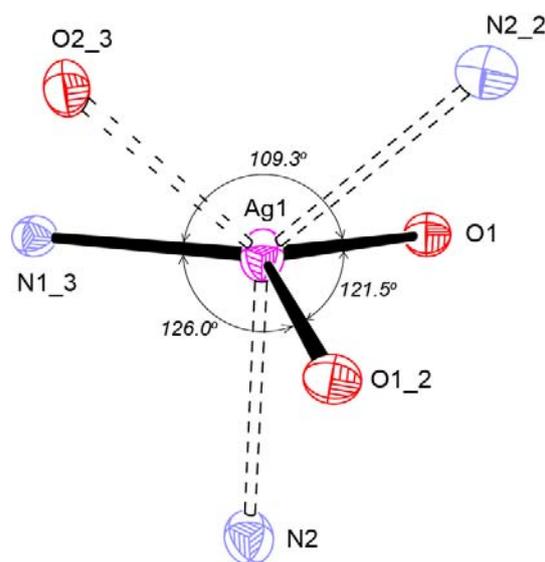
Details of geometry of the building block in the structure of Ag(PiCO) complex: anion and its closest Ag⁺ surrounding (A), and geometry of coordination polyhedron in the complex (B).

Symmetry codes for silver atoms in A: for Ag1 are x,y,z; for Ag1_1 are 1-x, -y,1-z; for Ag1_2 are 1-x, 1-y, 1-z; for Ag1_3 are x,1/2-y, 1/2+z.

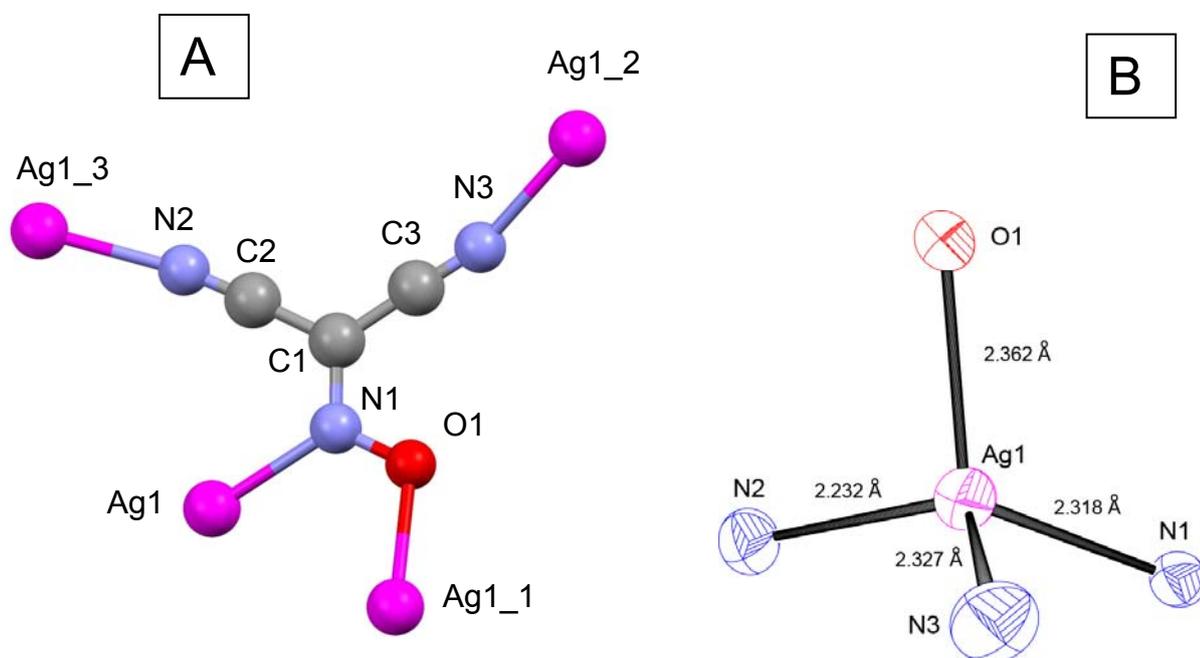
A



B

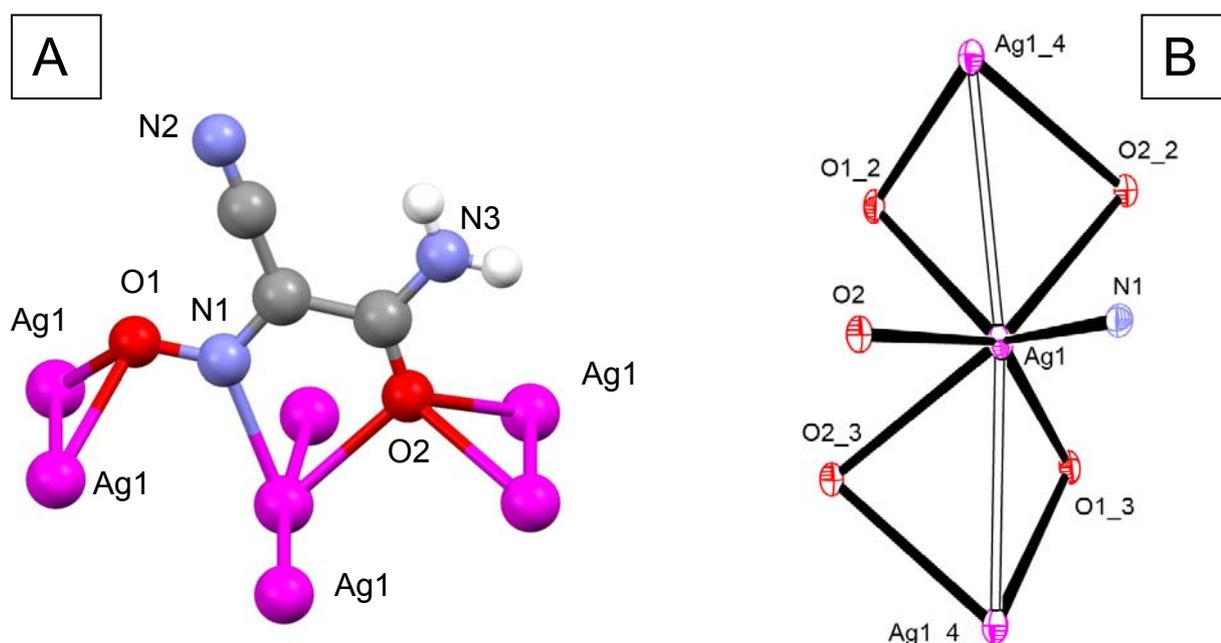


Details of geometry of the building block in the structure of Ag(CCO) complex: anion and its closest Ag⁺ surrounding (A), and geometry of coordination polyhedron in this complex (B).



Symmetry codes for silver atoms: #1 is 1-x, -y, 1-z; #2 is -1/2+x, y, 3/2-z; #3 is 1-x, 1-y, 1-z

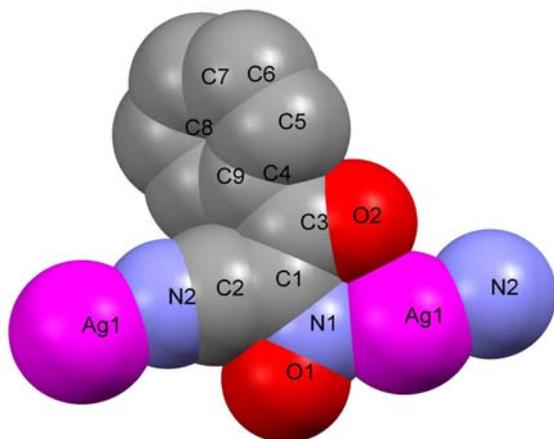
Details of geometry of the building block in the structure of Ag(ACO) complex: anion and its closest Ag⁺ surrounding (A), and geometry of coordination polyhedron in the complex (B).



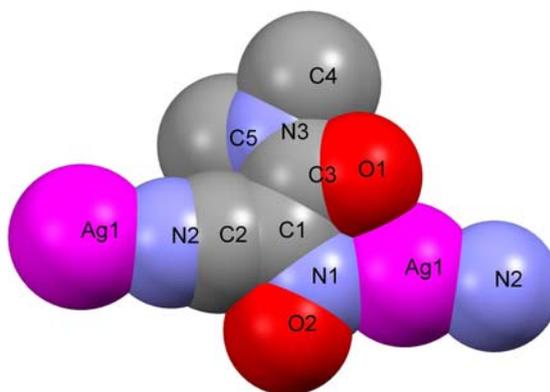
There are very close Ag---Ag distances in the structure of this complex equal to 3.194 Å due to specific arrangements of molecules during crystal packing in this layered structure. The distance Ag---Ag in metallic silver is 4.086 Å, while single bond was found to be 2.889 Å. Thus, observed in the Ag(ACO) structure distance is in the range of “argentophilic interactions” well documented in the literature. Most of crystallographic graphing software interprets this short distance as a bond, which is shown in the drawings above and in the main text (Figure 20 B).

Fragments of crystal structures of several AgL in a space-filing representation showing short, covalent bonds between silver and nitrogen atoms of the nitroso- and cyano- groups. H-atoms are omitted for clarity.

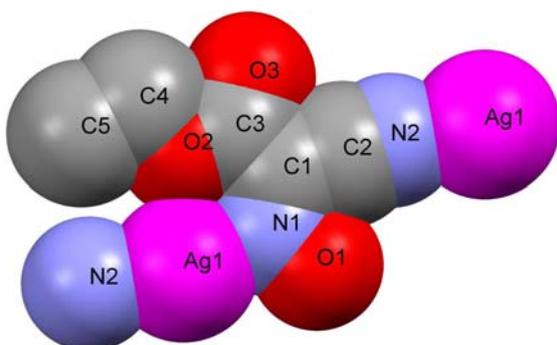
Ag(BCO)



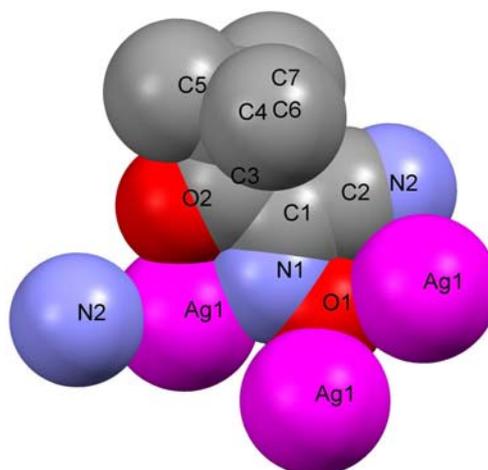
Ag(DCO)



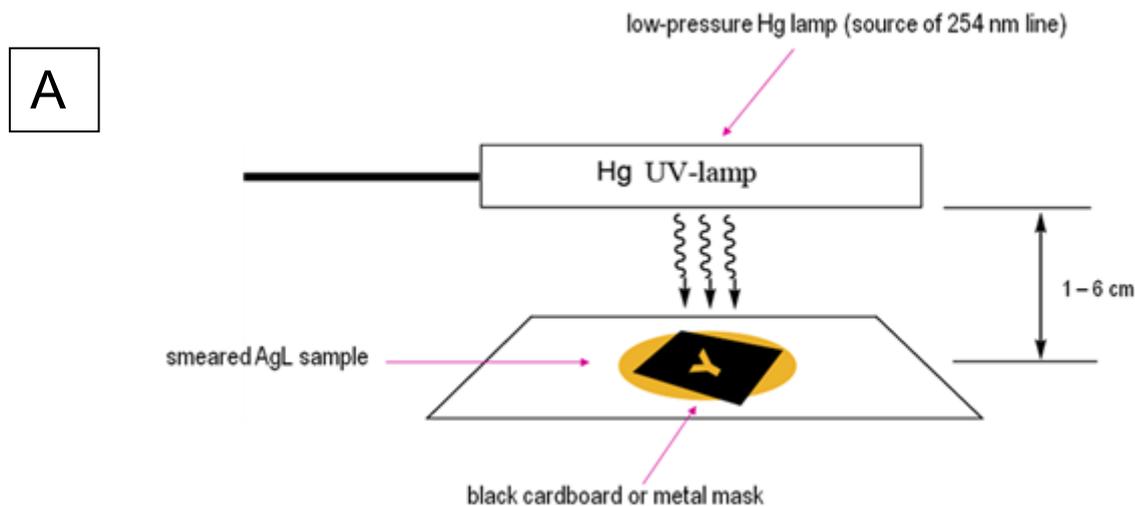
Ag(ECO)



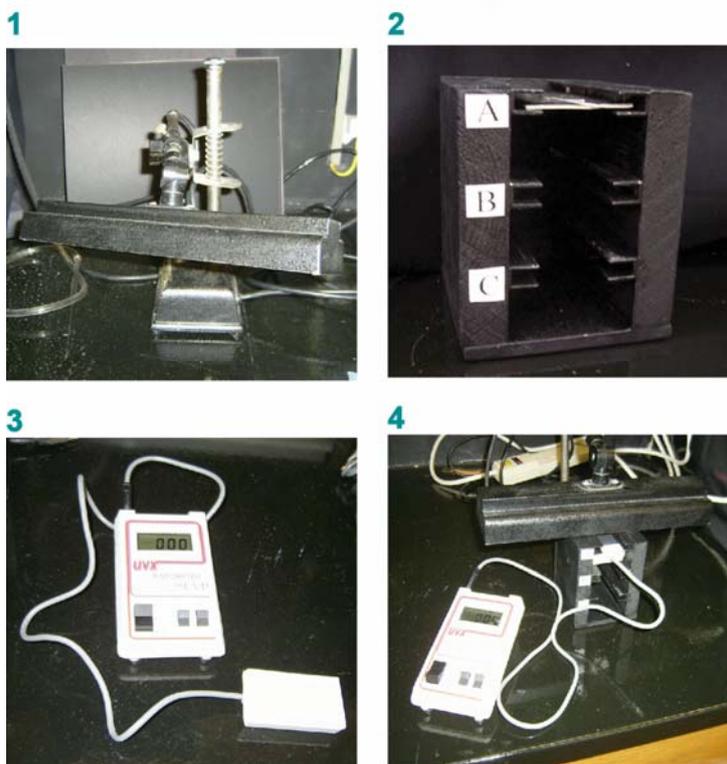
Ag(PiCO)



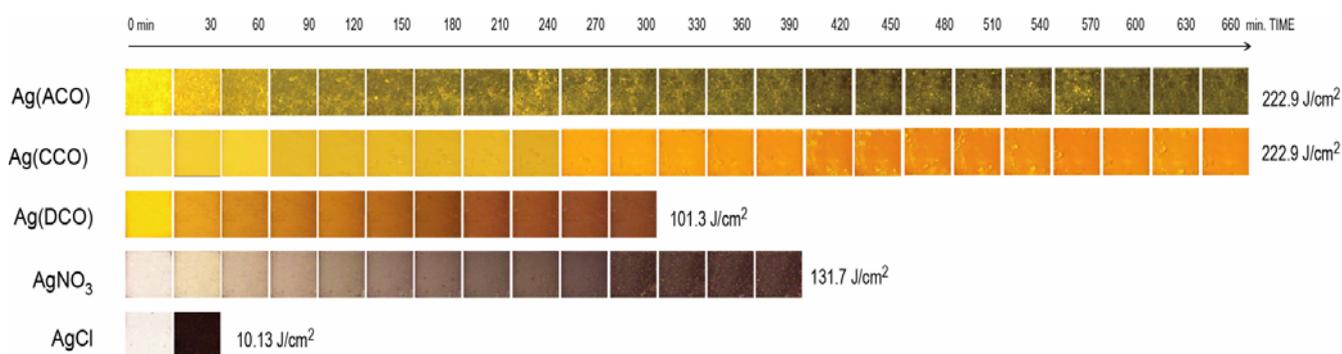
The experimental setup used for samples' UV-irradiation studies with the short wavelength (254 nm, low-pressure Hg lamp): **A** – conceptual diagram, **B** – actual laboratory setup showing the lamp, rack for holding samples at different heights, a UVX radiometer, and assembled system.



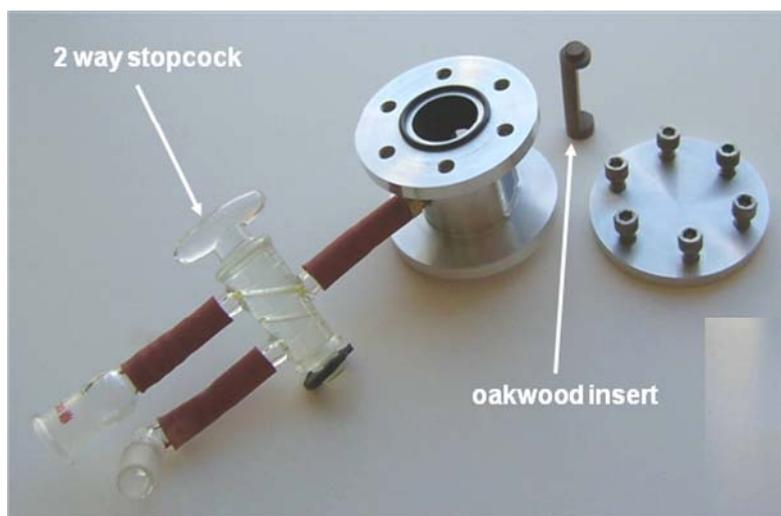
Hardware Setup:



Color palette observed for several AgL and common inorganic silver(I) salts (which were used as positive controls) upon exposure to UV-radiation with time. The source of radiation was low-pressure Hg lamp with the main output at 254 nm. The energy absorbed by samples at the point when no further color changes were detected is shown. High light sensitivity of AgCl and AgNO₃ is clearly seen in contrast to significantly more robust silver cyanoximates.



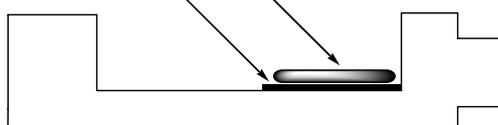
Custom built specialty gas cuvette for measurements of photoluminescence of solid samples in vacuum, or in the presence of different gases of industrial importance. An oak-wood was selected as an insert material due to its very low background (self-emission). Sample of AgL was ground in agate mortar and attached to the surface of the insert via double-sided tape as shown.



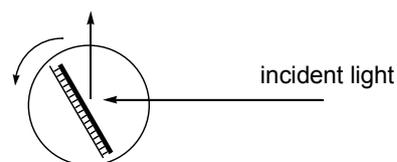
fine powder of solid AgL sample

double-sided adhesive 3M tape

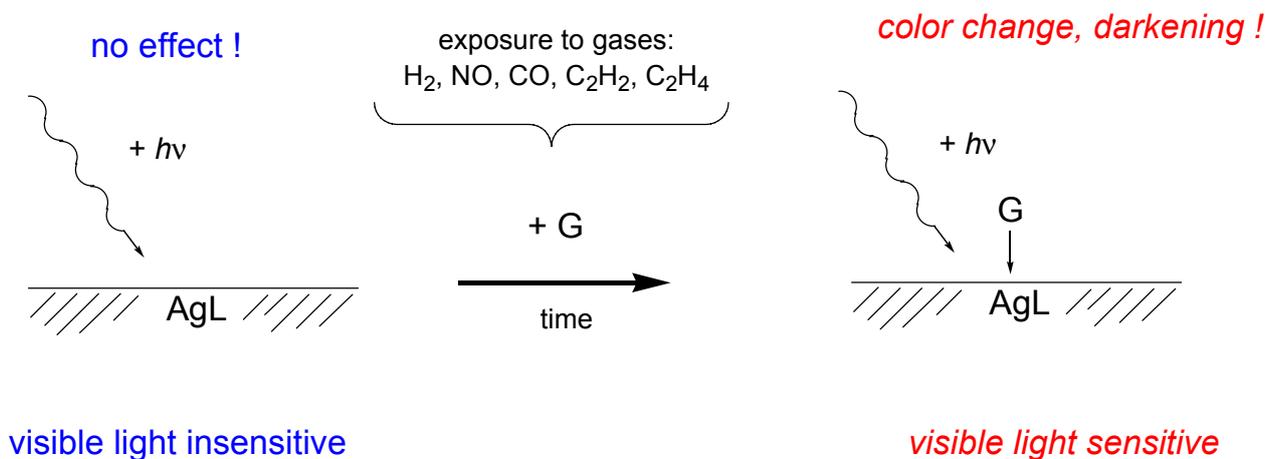
machined oak wood insert



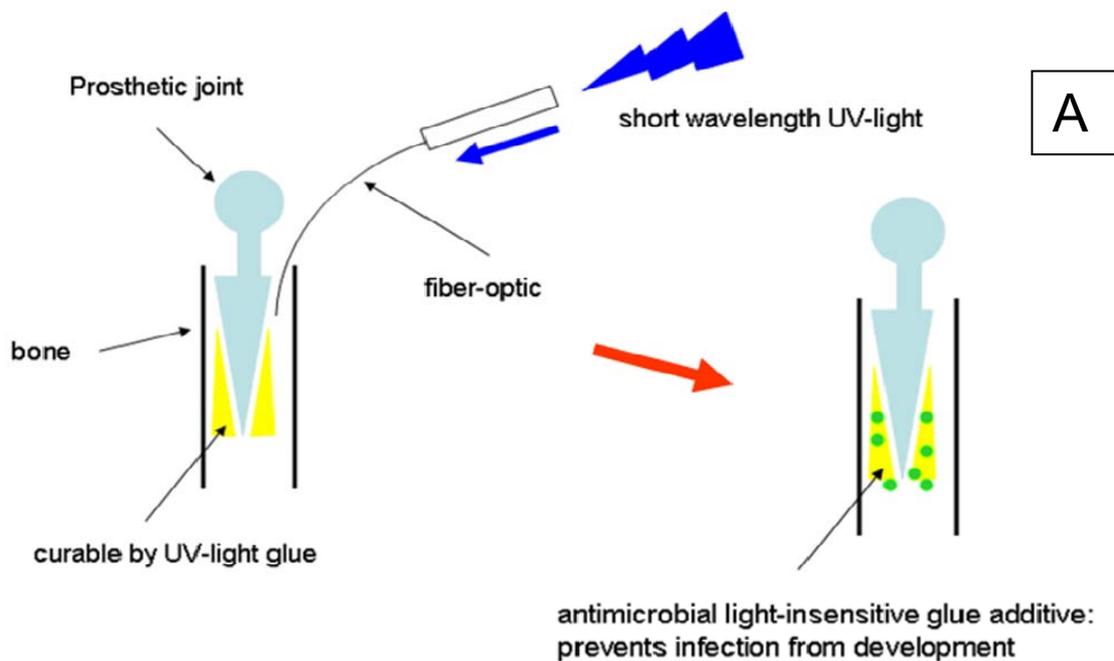
35, 45 and 55° positioning
with respect to the beam



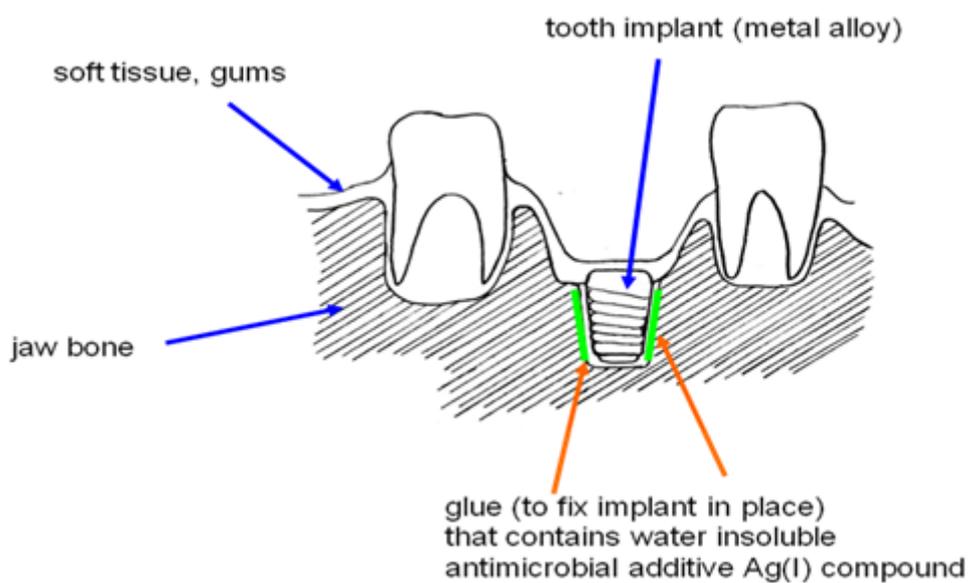
Surface sensitization in the presence of several gases of industrial importance: initially visible light insensitive AgL (A) after exposure to gases in the gas cuvette (ESI 24 above) to light at 300 nm (B), and after the removal of an insert and exposure of the sample to visible light (C). The coordination of gas molecules to AgL leads to the formation of complex on the surface of the sample, which now becomes light sensitive and darkens.



Conventional artificial joint insertion procedure and proposed addition of UV-light resistant antimicrobial silver(I) cyanoximate component (A), and similar application in dentistry (B).



B



Proof of concept: mixing of light-stable AgL with flowable polymeric resins commonly used in dentistry (**A**), and curing the mixture with conventional 400 nm visible light source that induces cross-linking in the composite (**B**).

