Crystal Structures of Ag(I) and Tl(I) Cyanoximates: Guide for Search for Light Insensitive Compounds, and Valuable Tool for Characterization of New Ligands.

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Monovalent silver and thallium have remarkably similar chemistry despite their different places in Periodic Table. Chemistry and applications of cyanoximes – new class of organic ampolidentate ligands – received considerable attention during the last two decades. These compounds have general formula NC-C(R)=NOH and there are currently 42 members in the series of cyanoximes [1]. We recently discovered that 12 cyanoximes form remarkably visible light insensitive, poor water soluble, thermally stable to 140ºC complexes and yet antimicrobial compounds [2]. The combination of the above properties made this group of twelve complexes of AgL composition unique (L = cyanoximes shown in Figure 1). The first quality of being light-stable complexes was explored in two areas of their practical application as colorimetric indicators that do not require an electric feed: 1) battery-less detectors of high-energy photons, and 2) non-electrical indicators for gases of industrial importance [3].

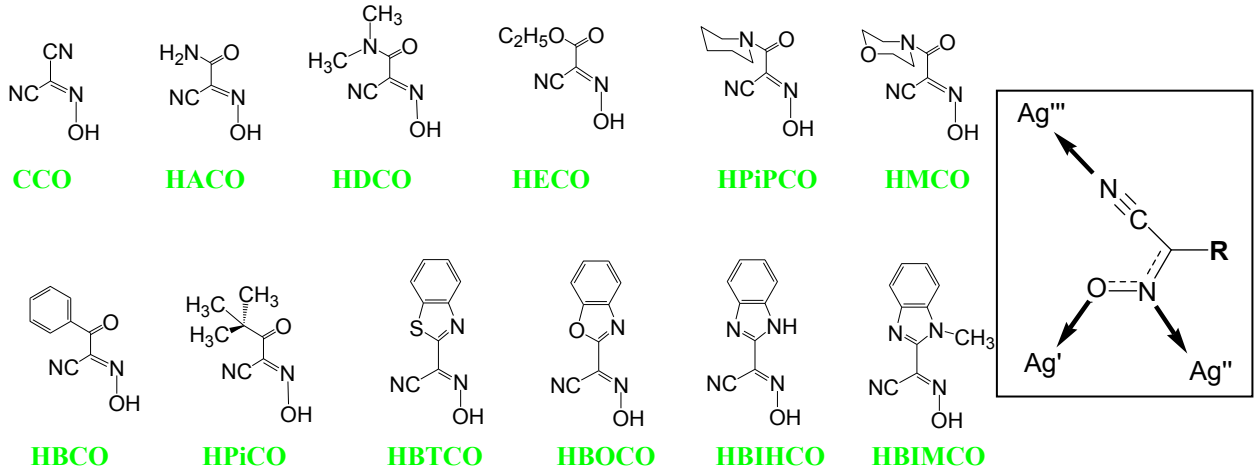

Fig 1. Chemical structures of cyanoximes that form light stable complexes of AgL composition (**A**) and deduced light insensitive motif (**B**).

Crystal structures of eight AgL complexes were determined and evidenced the formation of coordination polymers in which the cyanoxime anions act as bridging ligands of different complexity. There are short, covalent bonds between metal centres and N,O atoms of the bridging *nitroso*-group of the anion. Based on single crystal data a correlation between the rate of photodecomposition of AgL was established: longer Ag-N and Ag-O distances in bridging fragment (Figure 1B) lead to the greatest photostability of the complex. Data of structural studies were used to search and predict "light insensitive" structural motif for Ag(I) complexes with cyanoximes.

Thallium(I) complexes proved to be invaluable for two important purposes: 1) to remove halogen in numerous metathesis reactions instead of AgHal (Hal=Cl, Br, I) due to their high light sensitivity when the obtained products are unstable towards oxidizers; 2) to crystallize a variety of organic acido-ligands as TlL compounds and characterize in that way those species that otherwise very difficult to crystallize metal-free. The reaction between thallium carbonate and acido-ligands at ~95ºC leads to solutions of TlL as shown: $Tl_2CO_3 + 2\,HL = 2\,TlL + CO_2\uparrow + H_2O$. Slow cooling of those solutions always affords crystals suitable for the X-ray analysis. In all obtained Tl(I) cyanoximates ligands act as bridging anions by means of O,N atoms of the *oxime*-groups [4]. Hence, identification and characterization of new organic ligands is accomplished.

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3. N. Gerasimchuk, A.N. Esaulenko, K.N. Dalley, et al. *Dalton Trans*. **39**, 749 (2010)
4. N. Gerasimchuk, *Polymer*s, **3**, 2 (2011).