§5. Basic Studies of Electric Properties of Polymeric Silver(I) Complexes at Low Temperature

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The chemistry of coordination polymers has attracted much attention as they have potential as functional materials. Recently, a new simplified synthetic procedure for commercial manufacture of ternary single-source precursors (SSPs) to form polycrystalline AgIn*x*S*y* and CuInSe2 type semiconductors was reported [1]. We have been designing labile and antimicrobial active Ag-O and Ag-N bonding complexes. During the studies, we prepared water-soluble, relatively light-stable, chiral and achiral silver(I) complexes ($_\infty$\{[$Ag_2(ca)_2$]\} and $_\infty$\{[$Ag_2(ca)_2(Hca)_2$]\}), which exhibited extended linear Ag-Ag interactions (dotted lines in Fig. 1). Hence, we began to explore electrical properties of such coordination polymers having linear Ag-Ag interactions.

Last year, we grew needle crystals of $_\infty$\{[$Ag_2(ca)_2$]\} and $_\infty$\{[$Ag_2(ca)_2$ ($Hca)_2$]\}) on the slide glasses to measure electric resistances of these coordination polymer at low temperature. Electric resistances was estimated as 2.3MΩ at room temperature and 10MΩ at 77K using 0.1μA current source. The esd's of electric resistance were within 10% for three-times repeating, but voltage became larger in the fourth cycle of cooling.

In order to increase stability of the sample electrodes, water-insoluble linear silver(I) coordination polymers were prepared. We reacted several ligands (histidine, acetylhistidine, 4-aminomethylpyridine and 5,5'-bis-methyl-2,2-bipyridine) and silver sources (Ag_2O and $AgNO_3$) to synthesize water-insoluble coordination polymers ($_\infty$[Ag(his)](a)、 and $_\infty$[Ag(achis)] (b)) as well as known $_\infty$ [Ag_2(5,5'-bismethyl-2,2'-bpy) (4-amino-pyridine)]$(BF_4)_2$ (c) [2]. Except $_\infty$[Ag(achis)], obtained silver(I) complexes $_\infty$[Ag(his)] and [Ag_2(5,5'-bismethyl-2,2'-bpy)(4-aminopyridine)]$(BF_4)_2$ showed linear Ag-Ag interactions though the polymers. We are trying to grow crystals on glass plates suitable for electric resistance measurements.

[1] Kulbinder K. Banger, et al, *Inorg. Chem*., 2003, **42**, 7713-7715.
[2] Rodney P. Freazell et al, *Inorg. Chem*., 2006, **45**, 935-944.

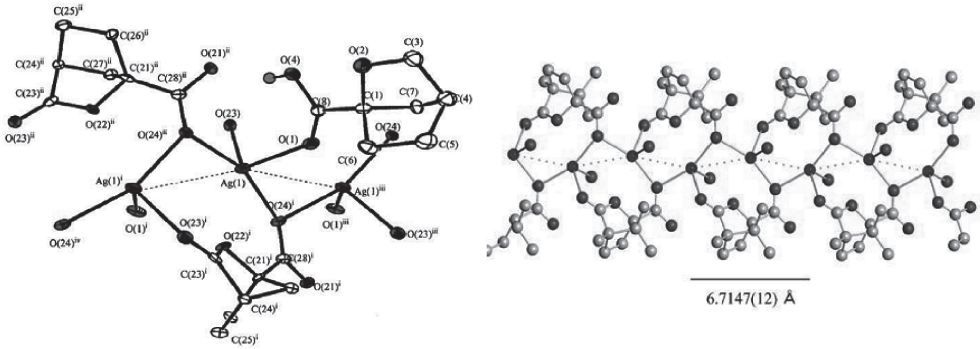

Fig. 1 Molecular structures of the local coordination around the silver(I) centers in the complexes.

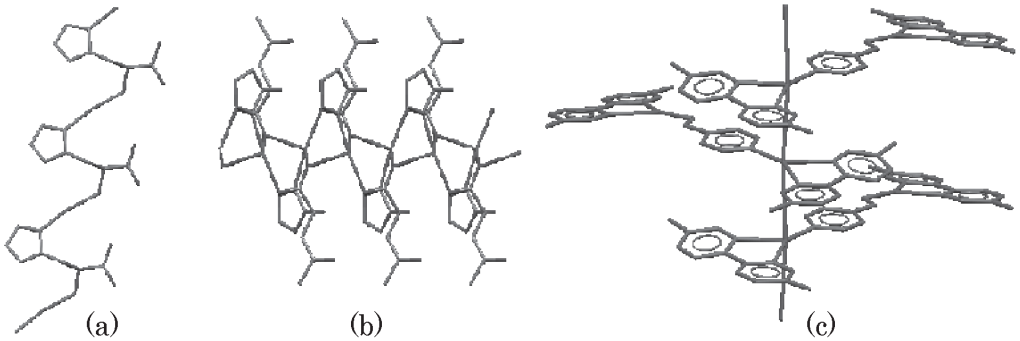

Fig. 2 Molecular structures of (a) $_\infty$[Ag(his)], (b) $_\infty$[Ag(achis)] (c) $_\infty$[Ag_2(5,5'-bismethyl-2,2'-bpy) (4-amino-pyridine)] $(BF_4)]_2$