An Order-Disorder Phase Transition in [Ag(bipy)NO₃]_n <u>Weenawan Somphon</u>^a, Kenneth J. Haller^a, A. David Rae^b, ^aSchool of Chemistry, Institute of Science, Suranaree Univ. of Tech., Nakhon Ratchasima 30000, Thailand. ^bResearch School of Chemistry, The Australian Univ., Canberra, ACT, 0200, Australia. E-mail: weenawanus@yahoo.com

The room temperature Fddd form of Ag(bipy)NO₃ contains a disordered NO3 ion and shows previously unreported planes of diffuse scattering indexed as $3k \pm l = 4n$ for the 296 K, a 12.8424(2), b 9.9429(1), c 34.4621(4) Å. Synthetic precession photographs showed the symmetry was Fddd at 160 K and above but a loss of systematic absences indicated F12/d1 (i.e. C2/c) at 150 K and below. The 100 K structure, C2/c, a 12.751(1), b 9.860(1), c 18.379(2) Å, β 109.98(1) ° has twin components related by a rotation around c*. The cell for F12/d1 has a' = a, b' = b, c' 34.547(2) Å, $\beta' 89.68(1)$ °. Refinement gave a 0.754(1):0.246 twin with no disorder and R(F) = 0.022 for 2294 obsd. rflns. Along a chain alternate, Ag atoms, (3b±c)/4 apart, are displaced 0.221(1) Å in opposite directions perpendicular to the chain. Chains are cross linked by Ag-Ag contacts of 2.958(1) Å and Ag–O contacts of 2.749(2) and 2.747(2) Å. The chains zig-zag so that Ag atoms avoid closer contact with the NO3. The 200 K structure, Fddd, a 12.823(1), b 9.937(1), c 34.450(1) Å was refined as a 1:1 disorder of all atoms initiated by disordering the 100 K structure. Constrained refinement gave R(F) = 0.028 for 1004 obsd. rflns. The Ag displacements reduced to $\pm 0.123(3)$ Å. The alternative orientation of the nitrate gave three Ag-O contact distances indicating an intermediate step for a change of local ordering. The diffuse scattering indicates that mistakes in NO3 positions cause a localized straightening of the adjacent chains that moves substantial amounts of these chains along their lengths. In contrast, the actual position of a nitrate only affects the closest Ag atoms.

Keywords: polymorphic structure, phase transition, orderdisorder transition