The aqueous solution chemistry of niobium is underexplored, and well characterized aqua complexes are scarce. In this contribution, a new niobium aqua complex was obtained by treatment of Zn-reduced ethanolic solution of NbCl$_5$ with HCl in the presence of aselenide source (ZnSe). This is the first example of selenium containing aqua complex of niobium. The yellow-green aqua complex was isolated by cation-exchange chromatography and transformed into corresponding isothiocyanate complex by ligand exchange, which was crystallized as (PyH)$_{4.5}$[H$_{4.5}$Nb$_4$SeO$_6$(NCS)$_{10}$]$\cdot$0.5H$_2$O. X-ray structural analysis revealed a metal-metal bonded tetranuclear{Nb$_4$(μ$_4$-Se)(μ$_2$-O)$_5$}$^{4+}$ core with a capping μ$_4$-Se ligand.