Catena structures formed by Li(+) with the TCNQF4(-) radical anion or with dianionic, diamagnetic TCNQF4(2-): Comparison to Cu(I)(TCNQX4) compounds (X = H, F, Cl)

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A series of compounds with chain structures, containing $Li^{(+)}$ and $TCNQF_4$, which is either monoanionic or dianionic ($TCNQF_4$ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) have been prepared using a simple diffusion-based technique and have been structurally characterized. Some of the compounds also contain nitrogen donor ligands such as bipy (bipy = 2,2'-bipyridyl). The radical anion $TCNQF_4^{(-)}$ is found in the compound Li(μ_3-$TCNQF_4$)(bipy), which was crystallized from acetonitrile. The crystal structure features a one-dimensional ribbon in which the $TCNQF_4^{(-)}$ radical anion bridges three $Li^{(+)}$ centers, each of which also has a chelating bipy. Another one-dimensional ribbon is found in the structure of $\{[(bipy)Li]_2\ (\mu_4\text{-}TCNQF_4)\}_n \cdot n$bipy, which has $TCNQF_4$ in its dianionic, diamagnetic form. Each $TCNQF_4$ fragment bridges four $Li^{(+)}$ centers, which are blocked by terminal chelating bipy groups that complete a tetrahedral environment around the $Li^{(+)}$ center. The structure will be compared to those of two $\{[Cu(I)bipy]_2(TCNQF_4)\}_n$ systems. [1] Crystals with a 3-D polymeric structure are formed by Li($TCNQF_4$), which is prepared in a two-step procedure. The crystal structure is similar to that reported for the Cu(I)-containing compound [Cu($TCNQH_2Cl_2$], for which remarkable physical properties were reported. [2]

References

{1} New $CuI_2(TCNQ^{-II})$ and $CuI_2(F_4TCNQ^{-II})$ Coordination Polymers. Brendan F. Abrahams, Robert W. Elliott, Timothy A. Hudson, Richard Robson, and Ashley L. Sutton. Cryst. Growth Des. ***2015****, 15, 2437−2444. DOI: 10.1021/acs.cgd.5b00220*

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