A chalcogen bond is an electrophilic interaction between an area of depleted electron density and elevated electrostatic potential (σ-hole) on a chalcogen atom, and an electron donor. Here, the preparation of a series of novel cocrystals featuring 3,4-dicyano-1,2,5-selenodiazole and of 3,4-dicyano-1,2,5-tellurodiazole as chalcogen bond donors and dimethyl sulfoxide & tetraphenylphosphonium bromide as chalcogen bond acceptors is reported. These novel cocrystals have been characterized by \(^{77}\text{Se}/^{125}\text{Te}\) solid-state NMR spectroscopy, single-crystal X-ray diffraction, and powder X-ray diffraction. The two σ-holes of each chalcogen in the donor molecules enable directional chalcogen-bond-driven cocrystallization with a range of electron donors. The halide acceptor, when cocrystallized with the chalcogen bond donor, exhibits two polymorphic forms as confirmed by single crystal X-ray structures. \(^{77}\text{Se}\) and \(^{125}\text{Te}\) solid-state NMR spectroscopy reveals in some cases an interesting spectral pattern where for one apparently crystallographically unique Se/Te site, a multiplet is observed. The possible origins of this complex multiplet are explored.