

Development of Novel Heterocyclic Compounds and Their Molecular Assemblies for Advanced Materials

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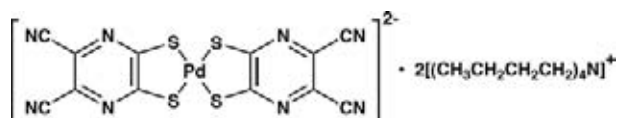
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Heterocycles containing sulfur and/or nitrogen atoms are useful as components of functional organic materials since heteroatoms in their rings are helpful to stabilize ions or ion-radical species. In addition, intermolecular interactions caused by heteroatom contacts can be expected to form unique molecular assemblies. In this project, novel functional organic materials based on various heterocycles were synthesized and their physical and structural properties were investigated.

1. Molecular and Crystal Structure of Bis(tetra-*n*-butylammonium) Bis(5,6-dicyanopyrazine-2,3-dithiolato- κ^2S,S') palladium(II)¹⁾

Metal dithiolene complexes have been widely investigated as molecular conductors and superconductors. Several superconductors and single-component molecular metals involving dithiolene complexes have been discovered to date. We have synthesized the title palladium dithiolene complex derived from 2,3-dicyano-5,6-dimercaptopyrazine ligand. The ligand is expected to extend the π -conjugation of the complex resulting in decreased Coulombic repulsion. Intermolecular interactions caused by $S\cdots S$ and $S\cdots N$ heteroatom contacts may increase the dimensionality in the solid state. In the complex the dianion molecule is located on an inversion center. The dianion is a flat molecule with an r.m.s. deviation of 0.034(8) Å of fitted atoms from the least-squares plane. The central Pd atom has a square-planar coordination geometry and the Pd–S distances and the S–Pd–S angle are 2.276(3), 2.294(3) Å and 89.39(10)°, respectively. These values are comparable to those found in bis(tetra-*n*-butylammonium) bis(4,5-dicyanobenzene-1,2-dithiolato- S,S')palladium(II) complex. The dianion mol-

ecules form a layered structure with an interlayer distance of 6.5 Å. The tetra-*n*-butylammonium cations are inserted between the layers.



2. Photoinduced Electron-Transfer Reaction of α -Bromomethyl-Substituted Benzocyclic β -Keto Esters with Amines: Selective Reaction Pathways Depending on the Nature of the Amine Radical Cations

Photoinduced electron-transfer reaction of α -bromomethyl-substituted benzocyclic β -keto esters with tertiary amines was investigated. Debrominated β -keto esters and ring-expanded γ -keto esters were obtained as major products. On the basis of mechanistic experiments it was concluded that these products are formed via a reaction sequence of selective carbon–bromine bond cleavage and subsequent competitive hydrogen abstraction and Dowd–Beckwith ring-expansion of the resulting primary alkyl radicals. The characteristic product distribution observed for the type of amine used is rationalized on the basis of selective reaction pathways of generated radical intermediates that depend on the nature of the amine radical cations.

Reference

- 1) M. Tomura and Y. Yamashita, *Acta Crystallogr., Sect. E: Struct. Rep. Online* **68**, m57–m57 (2012).