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Highly Polarizable Triiodide Anions (I_3^-) as Cross-Linkers for Coordination Polymers: Closing the Semiconductive Band Gap

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Supporting Information

ABSTRACT: From a hydrothermal reaction using CuI, KI, and 3,3′5,5′-tetramethyl-4,4′-bipyrazole (TMBP), the triiodide anion I_3^- has been integrated into the water-stable 2D coordination polymer Cu(TMBP)I_3 (**1**). In contrast with other metal triiodide complexes, **1** features remarkably small distortions in the bond distances associated with the I_3^- units (i.e., the Cu−I and I−I bonds), which effectively link up the copper(I) centers into infinite CuI_3 chains. The electronic band gaps and electrical conductivity data are also found to be consistent with the I_3^- ion acting as an effective linker across the copper(I) centers.

There is a recent surge of interest in the making of coordination polymers with significant semiconductive or electroactive properties.[1] A major motivation here is driven by the structural diversity imparted by the organic components, which provide rich potential for tailoring and exploring the electronic properties in the solid state. The structural diversity is readily seen in the various examples ranging from the close-packed (nonporous) rubeanatocopper(II) compounds,[2] copper 7,7,8,8-tetracyanoquinodimethane and related systems,[3] metal thioether/thiolate networks,[4] to the more recent open-framework/porous systems (e.g., the ones based on metal−sulfur links).[5]

However, among the widely studied coordination network systems,[1b,6] the semiconductive subclass is remarkably small, with the vast majority being decidedly insulators. Such an observation reflects the generally weak electronic interactions between the metal centers and organic linkers. To enhance the electronic interactions, it is helpful to utilize softer, more polarizable elements in the metal−organic bonding, for example, a sulfur donor often results in a smaller band gap than the oxygen and chloride counterparts.

In this context, the triiodide (I_3^-) ion presents a curious case. One the one hand, the iodide ion (I^-) as a soft species figures prominently in the construction of hybrid semiconductive materials, as is illustrated by the hybrid perovskites[7] and analogues[8] and their recent applications in solar cells.[9] Such remarkable electronic properties attest to the effective charge-transport pathway, as is provided by the iodo linkers across the metal centers. On the other hand, the larger and more polarizable triiodide anion as a bridging linker has remained conspicuously absent in the construction of coordination polymers. For example, a CCDC search (see Figure S1 in the Supporting Information, SI) for the M−I_3−M fragment (M: any metal) retrieved only several structures, but none of these features the I_3^- ion as an unbroken bridge across the metal centers: i.e., a large elongation is observed of either the M−I or I−I interactions, which effectively suppresses the cross-linking character of the triiodide units.

That is why we wish to draw attention to the triiodide as a distinct cross-linking unit, as observed in the 2D coordination network of Cu(TMBP)I_3 (**1**; TMBP = 3,3′5,5′-tetramethyl-4,4′-bipyrazole); Figure 1. The significant cross-linking character is

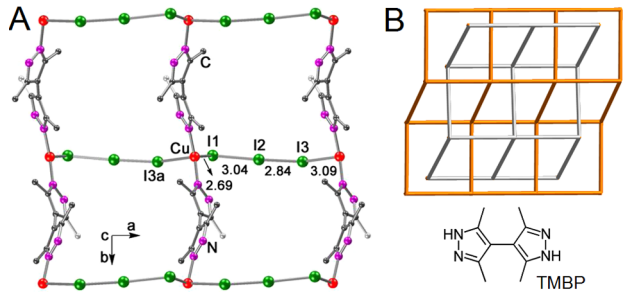

Figure 1. (a) View of a single sheet in **1** along the *c* axis (hydrogen atoms are omitted for clarity). (b) Schematic of the interlacing of two individual sheets in **1** (with the TMBP and I_3^- linkers simplified as struts). A drawing of TMBP is placed at the lower right.

reflected in the small variation of the Cu−I [e.g., 2.691 and 3.090 Å; cf. the van der Waals (VDW) contact for Cu−I, 3.41 Å[10]] and I−I (2.839 and 3.040 Å; cf. the VDW contact for I−I, 3.96 Å[10]) bond lengths. Compared with a monoiodide analogue, Cu(TMBP)I, previously reported,[11] Cu(TMBP)I_3 features a smaller band gap and greater conductivity, highlighting the effect of the more polarizable triiodide linker.

Compound **1** was obtained from a hydrothermal reaction of TMBP, CuI, and a large excess of KI (see the SI). The I_2 molecule was apparently generated from the in situ air oxidation of KI; e.g., the reaction mixture was stirred in air for 15 min before being loaded into the pressure reactor. The resultant black, needlelike

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crystals are air-stable and insoluble in water and common organic solvents. Single-crystal X-ray diffraction reveals that **1** features a 2D net (Figure 1a) formulated as $Cu(TMBP)I_3$, which crystallizes in the space group *Pbca*, with the asymmetric portion of the unit cell containing one CuI_3 fragment and a TMBP molecule. The 2D network features a nonplanar, corrugated shape that allows for two individual sheets to interlace, as is schematically represented in Figure 1b, with the copper center simplified as a nod and the TMBP and triiodide linkers as the struts. The two nets thus interlocked constitute a lamellar domain, and the lamellae are stacked along the crystallographic *c* axis to result in a close-packed structure with typical VDW contacts across the individual coordination grids.

As shown in Figure 1a, each copper(I) atom is four-coordinated in a distorted tetrahedral geometry, by two iodine atoms from two triiodide anions at Cu−I distances of 3.089(9) and 2.690(1) Å, respectively, and two nitrogen atoms from two separate TMBP molecules at Cu−N distances of 1.925(7) and 1.912(7) Å, respectively. Whereas the N−Cu−N angle is opened up to be 144.8°, the I−Cu−I angle (76.3°) is quite small, making for a distinct end-on I···I contact of 3.584 Å (shorter than the VDW distance of 3.96 Å[10]) across the two triiodine ligands around each copper(I) center. Each TMBP is electroneutral and bridges two metal centers, and the TMBP molecule features a dihedral angle of 57° between the pyrazole units. The combination of copper(I) centers and TMBP molecules forms zigzag chains extended along the *b* axis. The neighboring chains are linked by triiodide anions, resulting in a 2D corrugated network (Figures 1a and S2 in the SI). The interlinking triiodide anion is nearly linear (an I1−I2−I3 angle of 176.4°), with some distortions, as reflected in the bond length of I1−I2 (2.839 Å), being shorter than I2−I3 (3.039 Å).

To highlight the uniqueness of the interlinking, bridging character (i.e., across the two copper centers) of the triiodine ion in compound **1**, we present the three usable structures retrieved from the above-mentioned CCDC search for metal triiodide complexes. As is shown in Figure 2, the central iodine atom in

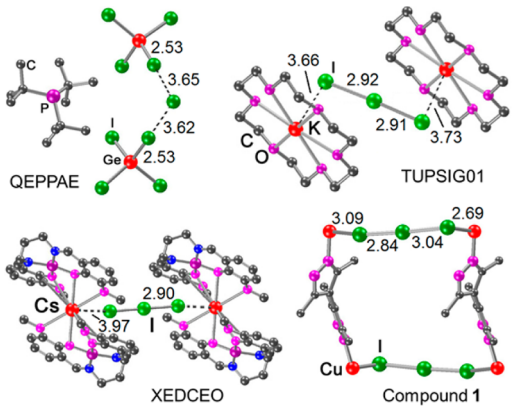

Figure 2. Local bonding features of the three crystal structures (containing I_3^- between metal centers) retrieved from the CCDC database, together with the local feature of **1**.

QEPPAE features the elongated I−I distances of 3.65 and 3.62 Å and can be considered rather as an isolated I^- ion in weak contacts with two GeI_4 species. On the other hand, the short I−I distances (2.90−2.92 Å) in TUPSIG01 and XEDCEO indicate well-defined triiodide (I_3^-) character, but these can be considered as isolated I_3^- ions charge-balanced by the very ionic K^+ and Cs^+ ions (as in the typical ionic compound of NaI_3), with little orbital overlap in between. In compound **1**, by contrast, the soft and highly polarizable copper(I) centers, together with the short I−I and Cu−I connections, present a unique case in which to probe the electronic interaction across the metal centers as well as throughout the solid state.

The phase purity and thermal stability of **1** were examined by powder X-ray diffraction (Figure S3) and thermogravimetric analysis (Figure S4), respectively. To probe the solid-state electronic properties, the diffuse-reflectance spectrum of a powder sample of **1** (spectrum c of Figure 3) was measured.

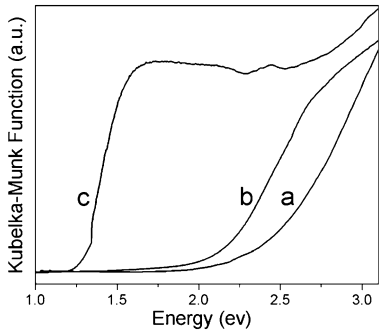

Figure 3. Room temperature optical absorption spectra for powder samples of (a) TMBP, (b) TCuI, and (c) **1**.

By fitting of the steepest slope on the absorption edge, on the basis of the Kubelka−Munk function, a band gap (E_g) of 1.28 eV (917 nm) was obtained for **1**. By comparison, a band gap of 2.15 eV (546 nm) was found from the diffuse-reflectance data (spectrum b of Figure 3) of the recently reported compound TCuI [composition: (TMBP)CuI], which is a 3D coordination polymer consisting of CuI chains integrated by the TMBP linkers (see Figure S5 in the SI for the crystal structure).[11] The significantly smaller electronic band gap in compound **1** is consistent with the integration of the triiodine anions as highly polarizable building blocks of the polymer grid. Such a contribution (toward reducing the band gap) from the triiodine anions apparently overrides the somewhat elongated Cu−I distances (2.691 and 3.090 Å) in compound **1** compared with those of TCuI (i.e., 2.678 and 2.802 Å).

Electrical conductivity measurement on the crystals of **1** also reveals its semiconductive nature. The needlelike single crystals of **1** facilitate measurement in the two-probe configuration. Thus, the sample exhibited a typical ohmic contact, yielding the conductivity value of 9.38×10^{-4} S m^{-1} (Figure S6 in the SI). By comparison, compound TCuI [composition: (TMBP)CuI, containing no I_3^- linkers] is an insulator, exhibiting a conductivity lower than 10^{-10} S m^{-1}. The greatly enhanced conductivity of **1** is consistent with the more polarizable nature of the I_3^- linker, and the consequently smaller electronic band gap, as seen in Figure 3. Further studies are being pursued on the electronic properties of compound **1**, which include a four-probe conductivity measurement to exclude the contact resistance and integration of the needle-shaped crystals into a field-effect transistor.

■ ASSOCIATED CONTENT

Supporting Information

Additional experimental procedures, full crystallographic data in CIF format, other related data, and photographs. The Supporting

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Notes

The authors declare no competing financial interest.

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