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Proton and Electron Transfer in the Formation of a Copper Dithiolene-Based Coordination Polymer

Stefan Henfling, Anastasia Kultaeva, Andreas Pöppl, Jennifer Klose, Berthold Kersting, Kostiantyn V. Domasevitch, and Harald Krautscheid*

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ABSTRACT: Metal bis(dithiolene) complexes are promising building blocks for electrically conductive coordination polymers. *N*-Heterocyclic dithiolene complexes allow their cross-linking via the coordination of N-donor atoms to additional transition metal ions. In this study, we present the formal copper(II) and copper(III) 6,7-quinoxalinedithiolene complexes $[Cu(qdt)_2]^-$ and $[Cu(qdt)_2]^{2-}$ (qdt²⁻: 6,7-quinoxalinedithiolate), as well as the 2D coordination polymer Cu[Cu(Hqdt)(qdt)] (3). The dithiolene complexes were isolated as $(Bu_4N)_2[Cu(qdt)_2]$ (1), Na[Cu(qdt)_2]·4H₂O (2a), $[Na(acetone)_4][Cu(qdt)_2]$ (2b), and $[Ni(MeOH)_6][Cu(qdt)_2]_2$ ·2H₂O (2c). Their crystal structures reveal nearly planar complexes with a high tendency of π -stacking. For a better understanding of their coordination behavior, the electronic properties are investigated by UV–vis–NIR spectroscopy, cyclic voltammetry, and DFT simulations. The synthesis of the 2D coordination polymer 3 involves the reduction and protonation of the monoanionic copper(III) complex. A combination of powder X-ray diffraction, magnetic susceptibility measurements, as well as IR and EPR spectroscopy confirm that formal



 $[Cu^{II}(Hqdt)(qdt)]^{-1}$ units link trigonal planar copper(I) atoms to a dense 2D coordination polymer. The electrical conductivity of 3 at room temperature is 2 × 10⁻⁷ S/cm. Temperature dependent conductivity measurements confirm the semiconducting behavior of 3 with an Arrhenius derived activation energy of 0.33 eV. The strong absorption of 3 in the visible and NIR regions of the spectrum is caused by the small optical band gap of $E_{g,opt} = 0.65$ eV, determined by diffuse reflectance spectroscopy. This study sheds light on the coordination chemistry of *N*-heterocyclic dithiolene complexes and may serve as a reference for the future design and synthesis of dithiolene-based coordination polymers with interesting electrical and magnetic properties.

INTRODUCTION

For almost six decades, square planar metal bis(dithiolene) complexes have been attracting great interest due to their outstanding and sometimes unusual optical, electrical, and magnetic properties.¹⁻⁴ They are characterized by an electronically delocalized $M(S_2C_2)_2$ core that can be further extended by various substituents. Often, dithiolene complexes can be isolated in a series with different total charges due to the ligands contributing to redox reactions. This behavior has been described as "non-innocence" and can be attributed to a similarity in energies of the metal and ligand frontier orbitals. $^{5-8}$ In N-heterocyclic dithiolene complexes, the electron transfer can further be coupled to the transfer of protons. $^{9-12}$ Metal dithiolene complexes find application in mainly two fields. First, especially N-heterocyclic dithiolene complexes serve in bioinorganic modeling studies, as the active sites of many metalloenzymes-like the molybdenum and tungsten-dependent oxidoreductases-contain metal dithiolene moieties.^{13,14} Second, dithiolene metal complexes are widely investigated for their potential application in electronic devices. Several compounds have been characterized as metallic molecular crystals^{15,16} or even superconductors.¹⁷⁻¹⁹ A detailed overview of conducting metal dithiolene complexes

has been provided by Kato.²⁰ Contrary to the numerous studies on the variation of counterions, there exist only a few reports that describe further coordination toward metal ions. The incorporation of metal dithiolene complexes as building blocks in conjugated coordination polymers could, however, lead to materials with interesting cooperative properties. Dithiolene based coordination polymers reported in the literature mostly consist of nitrogen containing dithiolene complexes, which are further coordinating to alkali metal ions.²¹⁻²⁹ In these cases, however, the interaction between nitrogen and alkali metal atoms is of a rather ionic nature, which limits through-bond charge delocalization. One example, which provided great incentive for research on transition metal ion based coordination polymers, was published by Takaishi et al.³⁰ They synthesized the first electrically conductive (6 \times 10^{-4} S/cm at 300 K) and porous coordination polymer

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Та	ble	e 1	. C	Crystal	and	Structure	Refinement	Data	of	1,	2b,	2c,	and	3
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compound	$(Bu_4N)_2[Cu(qdt)_2]$ (1)	$[Na(acetone)_4][Cu(qdt)_2]$ (2b)	$[Ni(MeOH)_6][Cu(qdt)_2]_2 \cdot 2 H_2O (2c)$	Cu[Cu(Hqdt)(qdt)] (3)			
space group	P2 ₁ /c	$P\overline{1}$	$P2_{1}/c$	P2 ₁ /c			
а	822.53(3) pm	830.54(3) pm	808.56(2) pm	432.695(8) pm			
Ь	1650.51(4) pm	969.33(2) pm	1797.12(3) pm	828.14(2) pm			
с	1868.12(6) pm	1021.13(3) pm	1588.62(4) pm	2208.82(7) pm			
α	90°	86.914(3)°	90°	90°			
β	92.860(3)°	81.084(3)°	98.124(2)°	95.799(1)°			
γ	90°	83.408(5)°	90°	90°			
volume/10 ⁶ pm ³	2533.0(1)	806.23(5)	2285.22(9)	787.44(4)			
Ζ	2	1	2	2			
Т	180 K	180 K	180 K	293 K			
R1 $(I > 2\sigma(I))$	0.029	0.031	0.033	$R_{\rm wp} = 0.033^{a}$			
wR2 (all data)	0.069	0.087	0.100	$R_{\rm p} = 0.026^{a}$			
a The structure was solved and refined using powder XRD data (Rietveld method).							

Cu[Cu(pdt)₂] (pdt²⁻: 2,3-pyrazinedithiolate). The copper(III) dithiolene complex [Cu^{III}(pdt)₂]⁻, reported by Ribas et al.,² served as a linker moiety. It bears four nitrogen donor coordination sites and can be reduced to the corresponding copper(II) complex at -0.72 V vs Fc/Fc⁺. Comproportionation with Cu^+ ions results in the formation of $Cu^{II}[Cu^{II}(pdt)_2]$. Just one year later, in 2010, Kobayashi et al. reported the isostructural coordination polymer Cu^{II}[Ni^{II}(pdt)₂].³¹ It exhibits permanent porosity, but a 4 orders of magnitude lower electrical conductivity with also a higher activation energy for charge transport. This may be explained by the weaker reducing power of $[Ni(pdt)_2]^{2-}$ compared to its copper analogue and the associated lower charge carrier delocalization in the coordination polymer.³² Since the building units are redox-active, the electrical conductivity could be increased by 4 orders of magnitude via partially oxidizing the framework with iodine to reach a value of 1×10^{-4} S/cm at 323 K (two-probe, film).³¹ Whereas the synthesis of $Cu^{II}[Cu^{II}(pdt)_2]$ and Cu^{II}[Ni^{II}(pdt)₂] includes the transfer of electrons, classical acid-base reactions may equally play an important role in the formation of N-heterocyclic dithiolene based coordination polymers. This was shown for the N–H protonated copper(I) complex $[Cu(H_2pdt)_2]^+$.¹² The reaction with additional Cu⁺ ions, in this case, leads to the 1D coordination polymer [Cu(Hpdt)] and is accompanied by a deprotonation of the H₂pdt ligands. Apart from the cited examples, dithiolene complexes have to date seldomly been used for the strategic design of transition metal ion-based coordination polymers. To explore the structure determining properties of dithiolene complexes in polymeric assemblies, we investigated the coordination behavior of the N-heterocyclic dithiolene complex $[Cu(qdt)_2]^ (qdt^2 : 6,7-quinoxalinedithiolate)$ toward Cu⁺ ions. In the first part, the manuscript focuses on the structural and electronic characterization of the formal copper(II) and copper(III) complexes $[Cu(qdt)_2]^{2-}$ and $[Cu(qdt)_2]^-$, isolated as $(Bu_4N)_2[Cu(qdt)_2]$ (1), Na[Cu- $(qdt)_2$]·4H₂O (2a), [Na(acetone)_4][Cu(qdt)_2] (2b), and $[Ni(MeOH)_6][Cu(qdt)_2]_2 \cdot 2H_2O$ (2c). The second part of this manuscript deals with the characterization of the physicochemical properties of the 2D coordination polymer Cu[Cu(Hqdt)(qdt)] (3).

RESULTS AND DISCUSSION

Synthesis. The synthesis of H_2 qdt (H_2 qdt: 6,7-quinoxalinedithiol) was performed according to the literature³³ with small variations that are described in the Supporting Information (chapter 1). Formal nickel(II) and nickel(III) dithiolene complexes with this ligand have been described by Das et al.^{33,34} Deprotonation of H_2 qdt with hydroxide ions and a subsequent reaction with Cu²⁺ ions resulted in the red complex $[Cu(qdt)_2]^{2-}$, isolated and characterized as $(Bu_4N)_2[Cu(qdt)_2]$ (1). Oxidation with iodine afforded the corresponding copper(III) complex, namely, the one-fold negatively charged green complex $[Cu(qdt)_2]^-$ which was identified by NMR spectroscopy (Figures SI-1, SI-2). It was crystallized as Na[Cu(qdt)₂]·4H₂O (2a) from a mixture of acetone/methanol (10:1, v/v) and as $[Na(acetone)_4][Cu (qdt)_2$ (2b) by diffusion of Et₂O into an acetone solution of **2a.** Concerning the coordination behavior of $[Cu(qdt)_2]^-$, we found that the diffusion-controlled reaction of 2a with certain divalent transition metal acetates in methanol resulted in the formation of crystalline materials. The dark, octahedral crystals of the reaction product with $Ni(OAc)_2 \cdot 4H_2O$ consist of $[Ni(MeOH)_6][Cu(qdt)_2]_2 \cdot 2H_2O$ (2c). The microcrystalline coordination polymer Cu[Cu(Hqdt)(qdt)] (3) was obtained by the solvothermal reaction of 2a with CuI and triphenylphosphine (PPh₃) in acetonitrile. The use of PPh₃ was required for the isolation of phase pure 3. If the synthesis of 3 is performed without PPh₃, qdt^{2-} is oxidized to the bisdisulfide $(qdt)_2$, while a coordination polymer similar to that of 3 is formed. The similar, but slightly larger unit cell and the absence of N-H stretching vibrations indicate the composition as $Cu_2[Cu(qdt)_2]$ (SI, chapter 8). Temperature dependent PXRD measurements of the coordination polymer 3 reveal its thermal stability up to 490 °C (Figure SI-21).

Crystal Structures of 1 and 2a–2c. Compounds 1 and **2a–2c** were characterized via single crystal X-ray diffraction and display structural properties that are typical for dithiolene complexes. The tetrabutylammonium salt of the copper(II) dithiolene complex 1 crystallizes in space group $P2_1/c$ (no. 14) with two formula units per unit cell (Table 1) and is isostructural to the previously reported nickel(II) analogue (Bu₄N)₂[Ni(qdt)₂].³³ The formal copper(II) atom exhibits a square planar coordination with the angle S1–Cu1–S2 = 90.24° (Figure 1). Selected bond lengths are summarized in Table SI-10. Compared to the average Ni–S distance in (Bu₄N)₂[Ni(qdt)₂] (216.9(2) pm), the Cu–S distances are considerably longer (Cu1–S1 = 225.91(5) pm, Cu1–S2 = 226.15(6) pm), but in good agreement with those of other homoleptic bis(dithiolene) copper(II) complexes.³⁵

Crystals of $Na[Cu(qdt)_2]$ ·4H₂O (2a) were obtained as intergrown dark green needles. Their diffraction data set only



Figure 1. Ellipsoid representation (50% probability) of the [Cu- $(qdt)_2$]²⁻ anion in 1. Symmetry code: a (2 - x, -y, 1 - z).

allowed the determination of a structure model, which is described in the SI (chapter 11). Slow diffusion of Et₂O into a solution of **2a** in acetone resulted, however, in prismatic, green crystals with good diffraction data quality. $[Na(acetone)_4]$ - $[Cu(qdt)_2]$ (**2b**) crystallizes in space group $P\overline{1}$ (no. 2) with one formula unit per unit cell (Table 1). The copper atom resides on an inversion center, and a perfectly planar coordination environment for the formal copper(III) atoms is observed (Figure 2a). The Cu–S distances are



Figure 2. (a) Ellipsoid representation (50% probability) of $[Cu-(qdt)_2]^-$ units in **2b**, linked by Na⁺ ions, which are coordinated by four acetone molecules each. Symmetry codes: a (2 - x, -y, 2 - z), b (1 - x, 1 - y, 1 - z). (b) $[Cu(qdt)_2]^-$ with viewing direction parallel to the short axis of the complex. (c) Schematic representation of the offset π -stacking interactions between the coordination chains in **2b**. The view is perpendicular toward the quinoxaline planes.

218.77(5) pm and 216.91(5) pm, about 8 pm shorter than in the corresponding copper(II) complex in 1, but similar to those reported in related copper(III) dithiolene complexes,^{24,36} and also similar to the Ni–S distance in the isoelectronic nickel(II) complex $(Bu_4N)_2[Ni(qdt)_2]$.³³ Besides the significant shortening of Cu–S bond lengths, the C–S and C1–C2 bond lengths change only slightly upon oxidation from the copper(II) to the copper(III) complex. A comparison of bond lengths in 1 and 2b is provided in Table SI-10. The distortion from planarity of the whole complex in 2b can be described by the angle δ between the least-squares planes spanned by the chelating unit C_2S_2 and the CuS_4 unit, being $9.54(5)^{\circ}$ (Figure 2b). The complexes are connected to chains in $[\overline{111}]$ direction by the coordination of the diagonal opposite nitrogen atoms N1 to sodium ions (Na1-N1 = 252.9(2) pm; Figure 2a). The sodium ions exhibit a slightly distorted octahedral coordination sphere with the oxygen atoms of two pairs of symmetry equivalent acetone molecules, occupying the equatorial positions of the NaN₂O₄ octahedron (Na1-O1 = 238.5(1), Na1-O2 = 247.8(2)). Each chain in **2b** is linked to two neighboring chains via offset $\pi \cdots \pi$ stacking interactions of the aromatic quinoxaline units with an atom to plane distance ranging from 328.8(8) pm to 334.5(2) pm (Figure 2c). As depicted in perpendicular view to the quinoxaline planes, the offset of the stacking is more dominant in the short axis of the quinoxaline units.

Single crystals of **2c** were obtained by the slow diffusion of $Ni(OAc)_2 \cdot 4H_2O$ into a solution of **2a** in methanol. As determined by X-ray single crystal structure analysis, this compound crystallizes in the monoclinic space group $P2_1/c$ (no. 14) with two formula units per unit cell (Table 1, Figure 3). Similar to the structure of **2b**, the complex is nearly planar with marginally varying Cu–S distances and S–Cu–S angles



Figure 3. (a) Ellipsoid representation (50% probability) of $[Cu-(qdt)_2]^-$ in **2c** with hydrogen bonds to methanol and water molecules. Symmetry codes: a (0.5 + x, 0.5 - y, -0.5 + z), b (1.5 - x, 0.5 + y, 1.5 - z). (b) Double layer of hydrogen bond connected dithiolene complexes in **2c**. The darker shaded complexes lie atop the brighter ones. The view is perpendicular to the planes of the complexes. Methyl groups, as well as hydrogen atoms that do not participate in hydrogen bonding, are omitted for clarity. (c) Stacking of $[Cu(qdt)_2]^-$ complexes between double layers, viewed in perpendicular direction to the plane of the complex. The darker shaded complex lies atop the brighter one. Hydrogen atoms are omitted for clarity.

ranging from 217.63(8) pm to 219.18(6) pm and 86.73(2)° to 91.59(2)°, respectively (Table SI-11). Curiously, the anionic complexes do not interact directly with the Ni²⁺ ions but are imbedded in an extended network of hydrogen bonds, π stacking, and weak intermolecular Cu-S interactions. Figure 3a displays hydrogen bonds of the complex with one water (O4b) and two methanol molecules (O1 and O2a). Donoracceptor distances are summarized in Table SI-12 and range between 272.7(3) pm and 282.2(3) pm. The Ni²⁺ ion, residing on an inversion center, is coordinated by three crystallographically different methanol oxygen atoms (O1, O2, O3) and exhibits a regular octahedral coordination. Ni-O distances lie in between 204.4(2) pm and 205.4(2) pm; O-Ni-O angles are close to 90° (Table SI-11). The hydroxy hydrogen atoms of four methanol molecules of each [Ni(MeOH)₆]²⁺ octahedron link the dithiolene complexes into an offset π stacked double layer (Figure 3b). The arrangement can be described as a herringbone motif, in which the complexes are packed with their long axis perpendicular to each other. The atom to plane distance between stacked quinoxaline groups is in the range of 348 to 359 pm. The double layers are stacked via additional $\pi \cdots \pi$ stacking interactions between adjacent quinoxaline units of 354.3(2) to 367.4(2) pm with a slightly lesser offset in both the short and the long axis of the ligand. This is shown in Figure 3c represented by two stacked dithiolene complexes belonging to adjacent double layers. Both shifts in the different $\pi \cdots \pi$ interactions can be explained by additional weak dipole-dipole interactions between copper and sulfur atoms. As represented in Figure 3b, copper and sulfur atoms in one double layer lie almost on top of each other with a distance of 338.52(1) pm. The shortest Cu-S distance between the double layers is slightly longer (350.32(1) pm). Both interatomic distances are longer than the sum of their van der Waals radii (320 pm).³

Electronic Properties of $[Cu(qdt)_2]^-$ and $[Cu(qdt)_2]^{2^-}$. Since the frontier molecular orbitals are essential to understanding the electrical and optical properties of dithiolene complexes, DFT calculations of $[Cu(qdt)_2]^-$ were performed at the B3LYP-D3BJ/ZORA-def2-TZVP level of theory. The geometry optimization of $[Cu(qdt)_2]^-$ in the gas phase reproduces well the experimentally determined bond lengths and angles of the complex in the solid state (Table SI-2). The slight overestimation of the M–S bond lengths of about 2.5 pm is not unusual for DFT calculations and has already been observed in similar systems.^{2,38–40} The HOMO (-2.69 eV) of $[Cu(qdt)_2]^-$ (Figure 4b) is a π orbital, extended over the whole complex. It consists of ligand p_z orbitals with a considerable contribution from the Cu d_{xz} orbital, antibonding



Figure 4. LUMO (a) and HOMO (b) of $[Cu(qdt)_2]^-$. The surface isovalue is 0.03.

with respect to the adjacent sulfur p_{z} orbitals. The LUMO (-0.69 eV; Figure 4a) is formed by the metal d_{xy} orbital and a combination of sulfur p_x and p_y orbitals, σ antibonding to the metal d_{vv} orbital. These findings are in line with molecular orbital representations of similar diamagnetic d^8 metal bis(dithiolene) complexes.^{24,39,41,42} The σ^* character of the LUMO is consistent with the about 8 pm longer Cu-S bond length, observed in the crystal structure of the reduced complex in 1. With regard to further investigations of the coordination chemistry, it is noteworthy that the lone pair electrons of sulfur atoms are mainly described by the HOMO (-2.69 eV), HOMO-1 (-3.13 eV), HOMO-2 (-3.28 eV), and HOMO-3 (-3.51 eV), whereas the unshared pair of electrons of the nitrogen atoms appear much more stabilized at the HOMO-5 (-4.35 eV), HOMO-6 (-4.36 eV), HOMO-13 (-5.98 eV), HOMO-14 (-6.03 eV), and HOMO-15 (-6.16 eV; Figure SI-3).

UV-vis-NIR absorption investigations of 1 and 2a uncover strong charge transfer excitations and support the delocalized electronic structure of both complexes. The electronic absorption spectrum of 2a in acetonitrile reveals two main excitations at 415 nm (log ε = 4.90) and 273 nm (log ε = 4.77) with shoulders directed toward higher energies (Figure 5).



Figure 5. UV–vis–NIR spectrum of **2a** in acetonitrile (solid line) and in methanol (dashed line).

Although the shoulder of the strongest absorption band is not well resolved in acetonitrile, it becomes more pronounced in the protic solvent methanol. Furthermore, the absorption at 415 nm displays an about 14 nm bathochromic shift when the solvent is changed from acetonitrile to methanol. An explanation might be that methanol molecules form hydrogen bonds with the electronegative nitrogen atoms of the quinoxaline unit, stabilizing the excited states of the dithiolene complex, and lowering the energy needed for the excitation.⁴³ TD-DFT simulations predict one-electron excitations at 250, 270, 311, 341, and 440 nm. The transitions are displayed as transition difference densities in Table SI-3. They visualize mostly ligand-to-metal charge transfer (LMCT) excitations, in which electron density is transferred from sulfur orbitals to the unoccupied Cu d_{xy} orbital, and metal-to-ligand charge transfer (MLCT), intraligand charge transfer (ILCT), and $\pi \rightarrow \pi^*$ transitions from the Cu d_{xz} and S p_z to the aryl p_z orbitals. Besides the absorption at the blue edge of the spectrum, 2a exhibits two weaker broad absorption bands at 608 nm (log ε = 2.58) and 1016 nm (log ε = 2.58; Figure SI-7).

In comparison to the green solution of **2a**, a solution of **1** in acetone appears red. The color is related to the absorption maximum at 466 nm for solutions of **1** (Figure SI-8, left). This bathochromic shift is explained by TD-DFT simulation of $[Cu(qdt)_2]^{2-}$ that predicts LMCT and MLCT transitions at 396 and 494 nm, respectively (Table SI-4). Exposed to air, the band at 466 nm successively vanishes, while the characteristic band for the copper(III) complex at 415 nm appears. The reaction proceeds within several minutes; isosbestic points evidence a constant stoichiometry and the direct transformation of $[Cu(qdt)_2]^{2-}$ to $[Cu(qdt)_2]^{-}$ (Figure SI-8, right).

The proton acceptor behavior of $[Cu(qdt)_2]^-$ was monitored by spectrophotometric titration experiments with aqueous hydrochloric acid. A good photometric response was observed in solutions of **2a** in acetone and DMSO (Figure SI-9). The decrease of the absorption at 420 nm was accompanied by the emergence of a new band at 479 nm in DMSO and 498 nm in acetone. Whereas the addition of 1 equiv of HCl to the acetone solution already induced a considerable change in the UV-vis-NIR spectrum, in DMSO, 15000 equiv was needed to observe a first effect. The isosbestic points suggest the direct protonation of $[Cu(qdt)_2]^-$ to [Cu(Hqdt)(qdt)]. By the addition of aqueous NaOH, this reaction is reversed.

The complex $[Cu(qdt)_2]^-$ not only accepts protons but also electrons. The cyclic voltammograms of 2a in the range of -2.0 to 0.25 V vs Fc/Fc⁺ (Figure 6) show two chemically



Figure 6. Cyclic voltammograms of 2a between -2.0 and 0.25 V vs Fc/Fc⁺ in DMSO at different scan rates.

reversible redox processes (p1, p2). The electrochemical parameters derived from the cyclic voltammetry studies are provided in Table SI-5. At $E_{1/2,p1} = -0.70$ V vs Fc/Fc⁺, $[Cu(qdt)_2]^-$ is reduced to $[Cu(qdt)_2]^{2-}$. Reduction potentials lower than -0.38 V vs Fc/Fc⁺ indicate the susceptibility to aerial oxidation of the reduced species.⁴⁴ This is consistent with the photometric response of solutions of 1 to aerial exposure. The difference between the reduction and oxidation potential of this redox event at $E_{1/2,p1}$ is 91 mV and does not change with the scan rate, indicating a fast electron transfer at the electrode. Both the oxidation and reduction reaction of p1 produce reaction products that do not precipitate on the electrode surface but remain in solution, as indicated by Randles-Ševčík plots (Figure SI-6).^{45,46} At $E_{1/2,p2} = -1.65$ V vs Fc/Fc⁺, a second redox process, p2, is observed. It is attributed

to the formation of the formal copper(I) species of the complex. The potentials for the current maxima and minima are separated by 161 mV at v = 25 mV/s. The distance increases with increasing scan rates. This is typical for a quasireversible electron transfer and slow kinetics at the electrode.⁴⁷ A structural change within the complex anion from a square planar to a tetrahedral coordination, typical for copper(I) complexes, might be a reason for the slow electron transfer. Scanning further anodically, one more-electron oxidation process starting at 0.25 V vs Fc/Fc⁺ can be observed and is represented in Figure SI-5. It appears irreversible and is combined with a chemical reaction and structural changes in the oxidized state. The formation of noninteger oxidation products has been found in other, similar dithiolene complexes.⁴⁸⁻⁵⁰ The reduction and redissolution of this oxidized species, covering the electrode, is observed in two steps at -1.0 and -1.1 V vs Fc/Fc⁺.

Concerning the electronic properties, significant similarities to literature known complexes should be pointed out. First, the observed reduction potential for $[Cu(qdt)_2]^-$ is the very same as that of its smaller analogue $[Cu(pdt)_2]^-$ (Figure SI-4).²⁴ It is, however, much more negative than that of the copper maleonitriledithiolate $[Cu(S_2C_2(CN)_2)_2]^{-/2-}$ couple $(E_{1/2} = -0.06 \text{ V vs Fc/Fc}^+)$,⁴⁴ which exhibits an air-stable dianionic form (Table SI-6). Compared to corresponding redox potentials of the copper dithiolene complexes $[Cu(S_2C_6H_4)_2]^$ and $[Cu(S_2C_6Me_4)_2]^-$, the observed reduction in $[Cu(qdt)_2]^$ occurs at less cathodic potentials (Table SI-6). The observed trend may be explained by the different extent of the electron withdrawing effect of different dithiolene ligand substituents. In general, substituents with stronger electron withdrawing properties cause a greater decrease in the energy of the frontier molecular orbitals and facilitate reduction processes. The reduced anionic complex is stabilized.^{41,51,52} Second, compared to the isoelectronic $[Ni(qdt)_2]^{2-}$, in which the redox active orbital is the HOMO,^{33⁻} in the CV of 2a, no reversible oxidation of the complex can be observed within the electrochemical window of DMSO. The redox active orbital in $[Cu(qdt)_2]^-$ is the LUMO. Since the HOMO in $[Ni(qdt)_2]^{2-}$ is delocalized over the whole complex, the ligand can be regarded as noninnocent in combination with nickel(II) atoms, whereas in combination with copper(III) atoms, the reduction takes place at the CuS₄ unit. The ligand can be considered innocent in this case.

Crystal structure of Cu[Cu(Hqdt)(qdt)] (3). The copper-(III) complex $[Cu(qdt)_2]^-$ served as a building block for the construction of the 2D coordination polymer Cu[Cu(Hqdt)-(qdt)] (3). The crystal structure of 3 was solved and refined on the basis of its powder X-ray diffraction pattern (Figure SI-22). Compound 3 crystallizes in the monoclinic space group $P2_1/c$ (no. 14) with one-half of the formula unit as an asymmetric unit (Table 1). Figure 7 shows the copper dithiolene complex with its connectivity toward the crystallographically different copper atoms (Cu1) on a general position. Free refinement of the Cu1 occupancy resulted in a value of 0.488(8) per formula unit and was set to 0.5, in agreement with the elemental analysis. Important bond lengths of the crystal structure are shown in Table SI-13. As expected, the overall D_{2h} symmetry of the dithiolene complex was retained, despite a slight distortion reflected in the Cu-S distances (Cu2-S1 = 229.1(5) pm and Cu2-S2 = 224.1(6) pm). Both bonds are longer than in the starting material 2a, where the average Cu-S distance is 217.8(9) pm. This is explained by



Figure 7. Coordination of the dithiolene complex in **3** to Cu1. The trigonally coordinated Cu1 atoms are in a general position with site occupation factor 0.5. Hydrogen atoms are omitted for clarity. Symmetry codes: a (-x, 1 - y, 1 - z), b (1 - x, 1 - y, 1 - z), c (1 - x, -y, 1 - z).

the reduction of the complex to a formal copper(II) dithiolene species with typical Cu-S distances of around 225.0 to 230.8 pm.⁵³ The other copper atoms, Cu1, are connecting the complexes in a trigonal planar coordination, distorted, however, toward pyramidal: Cu1 is located 23.0(7) pm above the plane spanned by the coordinating atoms N1c, S1b, and S2. The Cu1-N1c distance of 198(1) pm is, within the accuracy limits of powder diffraction data, similar to that of typical three coordinated copper(I) atoms with unsaturated nitrogen ligands (191–202 pm).^{54,55} Likewise, the Cu1–S bond lengths (Cu1-S1b = 221.5(9) pm, Cu1-S2 = 229(1)pm) are similar to literature reported Cu-S distances of trigonally coordinated copper(I) atoms (222-235 pm).⁵⁶⁻⁶¹ The Cu-Cu distances between the dithiolene copper atom Cu2 and the trigonally coordinated Cu1 alternate between 369.5(7) and 280.4(7) pm. The latter is surprisingly short and raises the question about the metal---metal interaction. Comparable short Cu…Cu distances of about 293 pm are reported for mixed-valence (Cu…Cu)³⁺ units in model systems of the biological Cu_A electron transfer site, a complex involved in the respiratory chain of eukaryotes.^{62,63} In these cases, both copper ions are bridged by two μ_2 thiolate functions and exhibit the same distorted tetrahedral coordination environment. The complexes are best described as delocalized mixed valence $Cu^{1.5}Cu^{1.5}$ systems. The structure of 3, on the contrary, exhibits distinct and typical coordination environments for Cu^I and Cu^{II}, which points toward a valence-trapped state, with no direct metal---metal interactions. Stibrany et al.⁶⁴ reported a similar system in which two distorted square planar cis-N(amine)₂S(thiolate)₂ coordinated copper(II) atoms and three trigonal planar S(thiolate)₂Cl coordinated copper(I) atoms are linked by μ_2 and μ_3 thiolate functions. The Cu^{II}...Cu^{II} distance in this case is 282.31(9) pm and similar to that observed in 3.64

Via the coordination to Cu1, a dense 2D network perpendicular to [001] is formed (Figure 8). All dithiolene units in one layer are oriented in the same direction and are stacked along the crystallographic *a* axis (Figure 8). The distance between parallel quinoxaline units is 341 pm. The offset of the π -stacking in 3 is predominant in the direction of the long axis of the complex (230 pm) and less along the short axis of the complex (90 pm)—resulting in a staircase like assembly in one stack (Figure 8b,c). The shortest Cu···S distance between adjacent complexes is 379.4(5) pm and is considerably longer than the sum of the atoms' van der Waals radii³⁷ (320 pm). As depicted in Figure SI-23, the layers are arranged in a staggered, interdigitated fashion to a densely



Figure 8. (a) Connectivity of dithiolene complexes via Cu1 (site occupation factor of 0.5) into a 2D network. (b) Stacking of dithiolene complex moieties in 3, viewed along their long axis, and (c) along their short axis. Hydrogen atoms are omitted for clarity.

packed structure. Besides weak van der Waals interactions, no further significant electronic attraction is observed between the layers.

Oxidation States in 3. The combination of magnetic susceptibility data, IR, and EPR spectra shows that copper(I) atoms are linked by protonated formally one-fold negatively charged copper(II) complexes, $[Cu^{II}(Hqdt)(qdt)]^-$. Evidence for the assumed protonation of one ligand was gained by IR spectroscopy of the deuterium labeled compound 3. The synthesis of the coordination polymer was executed in the presence of a small amount of D₂O to yield 3-D (Experimental Section). Phase purity was confirmed via X-ray powder diffraction (Figure SI-20). The N-H proton of $Cu^{I}[Cu^{II}(Hqdt)(qdt)]$ is considered acidic and expected to exchange with its heavier isotope, whereas C-H protons should remain unaffected. Figure 9 displays both IR spectra of



Figure 9. IR spectrum of **3** (black) and of its deuterated analogue **3-D** (red).

3 (black) and its deuterium exchanged analogue 3-D (red). The N-H stretching frequency in 3 of 3198 cm⁻¹ is lower than in most N-heterocycles, e.g., in pyrrole (3450 cm⁻¹).⁶⁵ It is, however, similar to the more acidic tetrazoles, which display N-H stretching frequencies at about 3145 cm⁻¹.⁶⁶ Assuming an equal bond strength for isotope exchanged bonds, the model of a harmonic oscillator predicts the stretching frequency of the heavier N-D couple at 2335 cm⁻¹. Since there are no other signals in this part of the spectrum, the appearance of the N-D stretching mode is clear and distinct

and is centered, close to the estimated value, at 2313 cm⁻¹. Below 1600 cm⁻¹, most frequencies remain unaffected upon deuteration. However, some of the bands lose intensity, while a few new ones appear at 1519, 1262, 772, and 627 cm⁻¹. They may be tentatively attributed to in plane and out of plane deformation vibrations involving H and D atoms.

These findings clearly show that the dithiolene coordination polymer **3** bears acidic N–H groups. EPR and magnetic susceptibility measurements indicate that the protonated dithiolene complexes additionally possess unpaired electrons and must have been reduced during the formation of **3**. The Xband cw EPR spectrum of a powder sample of **3** measured at 293 K (Figure 10) exhibits a typical anisotropic pattern for



Figure 10. X-band cw EPR spectrum of 3 at 293 K (black) and simulation (red).

Cu²⁺ (3d⁹, S = 1/2) in a magnetically nondiluted powder.^{67,68} The ^{63,65}Cu hyperfine interaction between the electron spin S = 1/2 and the nuclear spin $I^{Cu} = 3/2$ was not resolved due to the high metal atom concentration. In this case, the substantial magnetic exchange interactions between the neighboring copper(II) atoms average their nuclear spin configuration, and consequently the hyperfine splitting is not observed in the EPR spectrum.⁶⁸ The principal values of the Cu²⁺ g tensor, obtained by simulation, are $g_x = 2.020(1)$, $g_y = 2.022(1)$, and $g_z = 2.083(1)$, typical for a planar Cu^{II}S₄ coordination unit with D_{2h} symmetry or lower.^{69,70} The results of the EPR spectrum simulation support the assumption of a paramagnetic copper dithiolene species in **3**.

A variable temperature magnetic susceptibility measurement of 3 further corroborates that the coordination polymer contains paramagnetic copper(II) complexes and shows that they are antiferromagnetically coupled. Magnetic exchange interactions in 3 can be found in the a direction of uniformly stacked copper(II) complexes through Cu^{II}-S-Cu^I-S-Cu^{II} bonds with a syn-syn bridging mode. The through-space distance between the copper(II) centers is 432.70(1) pm. Additionally, each complex is linked statistically to two others of the two neighboring stacks via S–Cu^I–N bonds, resulting in Cu^{II}...Cu^{II} through-space distances of 828.14(2) pm and 934.37(2) pm (Figure SI-24). These magnetic interactions are, however, considered weak. In agreement with Cu1-S and Cu2–S bond lengths typical for oxidation states + I and + II, respectively, the effective magnetic moment μ_{eff} at room temperature is 1.61 $\mu_{\rm B}$ per Cu^I[Cu^{II}(Hqdt)(qdt)] formula unit and is slightly less than that of one noninteracting Cu²⁺ ion

(S = 1/2; μ_{eff} = 1.73 μ_{B} , g = 2.0). Upon cooling, the value gradually decreases to reach 0.43 μ_{B} at 2 K (Figure 11). This



Figure 11. Temperature dependence of the effective magnetic moment μ_{eff} (black squares) and the magnetic susceptibility (blue circles) for 3 at H = 0.5 T.

behavior is attributed to antiferromagnetic exchange interactions between the copper(II) complexes. The increase in $\chi_{\rm M}$ at low temperatures implies the presence of a paramagnetic impurity. A Curie-Weiss fit of the inverse magnetic susceptibility data of 3 from 300 to 70 K results in a Curie constant of C = 0.43 K and an asymptotic Curie temperature of Θ = -99 K (Figure SI-10). Taking into account the onedimensional stacking of Cu^{II} complexes, a fit of the magnetic susceptibility to the appropriate Bonner–Fisher model⁷¹ of an S = 1/2 infinite isotropic Heisenberg chain with the polynomial expression derived by Hall⁷² was attempted (Figure SI-11). Excluding the low temperature data and fixing g = 2.04 (derived by EPR spectroscopy), the least-squares fit resulted in a value of |J| = 58(1) cm⁻¹ for the electronic spin– spin coupling constant. The large coupling constant is not unusual for polymeric assemblies of dithiolene complexes. In the N-Cu^{II}-N bridged dithiolene coordination polymer Cu^{II}[Cu^{II}(pdt)₂],³⁰ the coupling constant between the dithiolene copper(II) atoms was determined to be 113 cm⁻¹, with q = 2.007.

Electrical Conductivity of Cu[Cu(Hqdt)(qdt)] (3). Metal bis(1,2-dithiolene) complexes are known for their extended frontier orbitals and the resulting delocalization of electrons. They have been intensively studied as molecular conductors and constitute a unique category of conducting materials.²⁰ The coordination polymer 3 bears one loosely bound unpaired electron in the formal copper(II) complex, which is expected to be further delocalized in the network via the coordination to copper(I) atoms. The electrical conductivity at 25 °C on a pressed pellet was measured with two contacts to be 2×10^{-7} S/cm. Compared to the reported dithiolene coordination polymer Cu[Cu(pdt)₂] ($\sigma = 6 \times 10^{-4}$ S/cm, 25 °C),³⁰ the electrical conductivity of 3 appears rather low. Since the herein described material shows connectivity only in two dimensions, the electrical conductivity is expected to display large anisotropy. This fact, as well as the presence of intergrain boundaries, limit the conductivity derived by measurements on a pellet. In a temperature dependent conductivity measurement, 3 was confirmed to be semiconducting with an Arrhenius temperature dependence (Figure SI-16). The activation energy derived from the linear region between 300 and 364 K is 0.33 eV. This is consistent with the optical band gap $E_{\rm g,opt} = 0.61$ eV, assigned by extrapolation of the absorption decay observed in the diffuse reflectance spectrum of **3** (Figure SI-17).

CONCLUSION

The copper quinoxalinedithiolene complex $[Cu(qdt)_2]^{-/2-}$ was explored for its structure directing properties in the formation of polymeric assemblies. Its planar structure, the extended π -system, and the polar Cu-S bonds make this dithiolene complex ideal for $\pi \cdots \pi$ and intermolecular Cu \cdots S interactions, as observed for 2a, 2b, 2c, and 3. Typical for dithiolene complexes, [Cu(qdt)₂]⁻ displays reversible oneelectron reduction processes at mild potentials, accompanied by small structural changes of the complex. This property, as well as the Lewis and the Brønsted basicity of the nitrogen atoms in $[Cu(qdt)_2]^-$, have been shown to play all together an important role in the formation of compound 3. In the synthesis of 3, the copper(III) complex $[Cu(qdt)_2]^-$ is reduced and protonated at one nitrogen atom. The resulting paramagnetic dithiolene complex anions are linked by trigonally planar coordinated copper(I) atoms to a dense 2D coordination polymer with antiferromagnetic exchange interactions and a room temperature electrical conductivity of 2 \times 10^{-7} S/cm.

This study presents a large variety of parameters to address for a strategic synthesis of polymeric dithiolene structures. We anticipate that dithiolene complexes will be more widely perceived as tunable building blocks for the synthesis of moredimensional coordination polymers with highly interesting electronic and magnetic properties.

EXPERIMENTAL SECTION

Experimental details and the synthesis of H_2qdt are provided in the Supporting Information.

 $(Bu_4N)_2[Cu(qdt)_2]$ (1). H_2qdt (1.36 g, 7.0 mmol, 1 equiv) was deprotonated with KOH (786 mg, 14.0 mmol, 2 equiv) in 40 mL of methanol and 40 mL of acetone. To the red solution, a solution of CuCl₂·2H₂O (597 mg, 3.5 mmol, 0.5 equiv) in 10 mL of methanol was added dropwise. The solution was filtered, and 2.42 g (7.5 mmol, 1.1 equiv) of (Bu₄N)Br was added. After removal of the solvent, the red solid was extracted with 100 mL of acetone. Layering with diethyl ether resulted in dark red needle-shaped crystals of 1.

Yield: 1.92 g, 2.1 mmol, 59%. $T_{\rm m}$: 181 °C. EA, found: C, 61.16%; H, 8.45%; N, 8.94%. Calculated for $(C_{48}H_{80}N_6S_4Cu)$: C, 61.78%; H, 8.66%; N, 9.01%. HR-MS (ESI): m/z 446.893 [Cu(qdt)₂]⁻. UV/vis/ NIR (acetone): λ [nm] (log ε) = 479 (4.71). IR (KBr): $\tilde{\nu}$ [cm⁻¹] 3009 (w), 2957 (m), 2934 (m), 2871 (m), 1560 (w), 1469 (m), 1454 (m), 1435 (s), 1410 (s), 1378 (m), 1361 (w), 1340 (m), 1329 (w), 1269 (w), 1218 (w), 1177 (s), 1156 (s), 1122 (w), 1073 (s), 1029 (s), 977 (w), 932 (m), 900 (w), 878 (m), 801 (w), 785 (m), 744 (m), 668 (m), 630 (w), 604 (m), 523 (w), 526 (w), 482 (w), 435 (w).

Na[Cu(qdt)₂]·4H₂O (2a). H₂qdt (1.89 g, 9.73 mmol, 1 equiv) was suspended in 68 mL of degassed acetonitrile and deprotonated with an aqueous solution of 2 M NaOH (14 mL, 28 mmol, 2.9 equiv). After 3 h of vigorous stirring, $Cu(ClO_4)_2$ ·6 H₂O (1.80 g, 4.86 mmol, 0.5 equiv) was added to the brown slurry to afford a dark red solution. Iodine (617 mg, 2.43 mmol, 0.25 equiv) was added, and the solvent was removed under reduced pressure. The resulting dark brown precipitate was redissolved in 85 mL of methanol. After stirring for 4 h at room temperature in an open beaker, a dark crystalline precipitate formed from the red solution. It was filtered off and dried under reduced pressure. The crude product was dissolved in 150 mL of acetone and filtered through a bed of Celite. The dark green solution was diluted with 40 mL of methanol and concentrated under vacuum

at 40 °C until the first small crystals appeared. Crystallization was completed overnight at 6 °C. After filtration and washing with cold methanol and diethyl ether, dark green crystals of compound 2a were isolated.

Yield: 835 mg, 1.54 mmol, 32%. EA found: C, 35.58%; H, 2.74%; N, 10.45%. Calculated for $(C_{16}H_{16}N_4S_4O_4CuNa)$: C, 35.38%; H, 2.98%; N, 10.32%. HR-MS (ESI): m/z 446.893 $[Cu(qdt)_2]^-$. ¹H NMR (400 MHz, DMSO-d₆): δ [ppm] 7.62 (s, 2 H, CH_{arom}), 8.64 (s, 2 H, CH_{arom}). ¹³C NMR (100 MHz, DMSO-d₆): δ [ppm] 122.8 (s, 2 C, C_{arom}), 140.4 (s, 2 C, C_{arom}), 143.2 (s, 2 C, C_{arom}), 152.3 (s, 2 C, C_{arom}). UV/vis/NIR (acetonitrile): λ [nm] (log ε) 273 (4.77), 415 (4.90), 608 (2.58), 1016 (2.58). IR (KBr): $\tilde{\nu}$ [cm⁻¹] 3510 (m), 3342 (m), 3186 (m), 1644 (m), 1454 (s), 1422 (m), 1354 (s), 1334 (m), 1182 (s), 1149 (w), 1101 (s), 1037 (s), 978 (w), 930 (m), 880 (m), 791 (m), 673 (m), 626 (w), 419 (m).

[Na(acetone)₄**][Cu(qdt)**₂**] (2b).** Crystals of **2b** were obtained via slow diffusion of diethyl ether into a solution of **2a** in acetone.

 $[Ni(MeOH)_6][Cu(qdt)_2]_2 \cdot 2H_2O$ (2c). A 2 mL glass vial with $Ni(OAc)_2 \cdot 4H_2O$ (6.2 mg, 0.025 mmol, 1 equiv) was placed in a 20 mL glass vial with 2a (13.6 mg, 0.025 mmol, 1 equiv). Both were filled slowly with methanol. After 1 week, black crystals of 2c formed on the outer wall of the small vial.

Cu[Cu(Hqdt)(qdt)] (3). A Teflon lined steel autoclave was loaded with 2a (54.3 mg, 0.10 mmol, 1 equiv) and a solution of CuI (19.0 mg, 0.10 mmol, 1 equiv) and Ph_3P (104.9 mg, 0.40 mmol, 4 equiv) in 15 mL of acetonitrile. The autoclave was sealed, and the reaction mixture was heated to 100 °C within 20 h. The temperature was kept at a constant level for 1 h before cooling the autoclave to room temperature during a period of 2 h. The resulting black microcrystal-line solid was isolated via decantation. The product was washed thoroughly with acetonitrile and methanol before being dried under reduced pressure.

Yield: 40 mg, 0.078 mmol, 78%. EA found: C, 37.67%; H, 1.67%; N, 10.79%, S: 24.89%, Cu: 24.9%. Calculated for $(C_{16}H_9Cu_2N_4S_4)$: C, 37.48%; H, 1.77%; N, 10.93%, S: 25.02, Cu: 24.79%. IR (KBr): $\tilde{\nu}$ [cm⁻¹] = 3197 (w), 3082 (w), 3040 (w), 3020 (w), 1590 (w), 1551 (m), 1467 (w), 1446 (s), 1438 (s), 1404 (m), 1370 (w), 1353 (m), 1337 (m), 1313 (m), 1313 (m), 1219 (m), 1203 (s), 1189 (m), 1175 (s), 1081 (s), 1055 (w), 1038 (m), 979 (w), 928 (w), 876 (m), 860 (m), 781 (m), 763 (w), 752 (w), 672 (w), 666 (w), 616 (w), 596 (w), 540 (w), 502 (w), 429 (m).

Cu[Cu(Dqdt)(qdt)] (3-D). On the basis of the synthetic protocol of compound 3, two drops of D_2O were added to the reaction mixture before the autoclave was heated in the oven.

IR (KBr): $\tilde{\nu}$ [cm⁻¹] 3198 (w), 3084 (w), 3036 (w), 3021 (w), 2313 (w), 1590 (w), 1550 (m), 1519 (m), 1446 (s), 1439 (s), 1405 (m), 1353 (m), 1321 (m), 1264 (m), 1207 (s), 1173 (m), 1080 (s), 1038 (m), 979 (w), 959 (w), 928 (w), 875 (m), 854 (m), 772 (m), 666 (m), 627 (w), 616 (w), 589 (w), 540 (w), 502 (w), 429 (m).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00914.

Details concerning the experimental part and ligand synthesis, NMR spectroscopy, DFT calculations, cyclic voltammetry, UV–vis–NIR spectroscopy, EPR spectroscopy, magnetic characterization, influence of PPh₃ in the formation of **3**, electrical conductivity measurement, diffuse reflectance spectroscopy, single crystal structure analysis, and X-ray powder diffraction and Rietveld refinement (PDF)

Accession Codes

CCDC 2065438–2065442 contain the supplementary crystallographic data for compounds 1, 2b, 2c, 3 and $(qdt)_2$. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data request/cif, or by emailing data request@ccdc.cam.ac.

uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Harald Krautscheid – Institute for Inorganic Chemistry, Universität Leipzig, D-04103 Leipzig, Germany;
orcid.org/0000-0002-5931-5440; Email: krautscheid@ rz.uni-leipzig.de

Authors

Stefan Henfling – Institute for Inorganic Chemistry, Universität Leipzig, D-04103 Leipzig, Germany

- Anastasia Kultaeva Felix Bloch Institute for Solid State Physics, Universität Leipzig, D-04103 Leipzig, Germany; Faculty of Chemistry and Biochemistry, Ruhr University Bochum, D-44801 Bochum, Germany
- Andreas Pöppl Felix Bloch Institute for Solid State Physics, Universität Leipzig, D-04103 Leipzig, Germany; orcid.org/0000-0003-2354-2542
- Jennifer Klose Institute for Inorganic Chemistry, Universität Leipzig, D-04103 Leipzig, Germany
- Berthold Kersting Institute for Inorganic Chemistry, Universität Leipzig, D-04103 Leipzig, Germany
- Kostiantyn V. Domasevitch Department of Inorganic Chemistry, University of Kiev, UA-25033 Kiev, Ukraine; orcid.org/0000-0002-8733-4630

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.1c00914

Author Contributions

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Robertson, N.; Cronin, L. Metal bis-1,2-dithiolene complexes in conducting or magnetic crystalline assemblies. *Coord. Chem. Rev.* **2002**, 227 (1), 93–127.

(2) Ray, K.; Weyhermüller, T.; Neese, F.; Wieghardt, K. Electronic structure of square planar bis(benzene-1,2-dithiolato)metal complexes $[M(L)_2]^z$ (z = 2–, 1–, 0; M = Ni, Pd, Pt, Cu, Au): an experimental,

density functional, and correlated ab initio study. *Inorg. Chem.* 2005, 44 (15), 5345-5360.

(3) Stiefel, E. I. *Dithiolene Chemistry*; John Wiley & Sons, Inc, 2003. DOI: 10.1002/0471471933.

(4) Rauchfuss, T. B. Synthesis of Transition Metal Dithiolenes in Dithiolene Chemistry. In *Dithiolene Chemistry*; Stiefel, E. I., Ed.; John Wiley & Sons, Inc, 2003; pp 1–54.

(5) Ward, M. D.; McCleverty, J. A. Non-innocent behaviour in mononuclear and polynuclear complexes: consequences for redox and electronic spectroscopic properties. *J. Chem. Soc., Dalton Trans.* **2002**, *3*, 275–288.

(6) Butin, K. P.; Beloglazkina, E. K.; Zyk, N. V. Metal complexes with non-innocent ligands. *Russ. Chem. Rev.* 2005, 74 (6), 531–553.

(7) Coucouvanis, D.; Paital, A. R.; Zhang, Q.; Lehnert, N.; Ahlrichs, R.; Fink, K.; Fenske, D.; Powell, A. K.; Lan, Y. Synthesis, electronic structure, and structural characterization of the new, "non-innocent" 4,5-dithio-catecholate ligand, its metal complexes, and their oxidized 4,5-dithio-o-quinone derivatives. *Inorg. Chem.* **2009**, *48* (18), 8830–8844.

(8) Eisenberg, R.; Gray, H. B. Noninnocence in metal complexes: a dithiolene dawn. *Inorg. Chem.* **2011**, *50* (20), 9741–9751.

(9) Kimura, Y.; Hayashi, M.; Yoshida, Y.; Kitagawa, H. Rational Design of Proton-Electron-Transfer System Based on Nickel Dithiolene Complexes with Pyrazine Skeletons. *Inorg. Chem.* 2019, 58 (6), 3875–3880.

(10) Kennedy, S. R.; Goyal, P.; Kozar, M. N.; Yennawar, H. P.; Hammes-Schiffer, S.; Lear, B. J. Effect of Protonation upon Electronic Coupling in the Mixed Valence and Mixed Protonated Complex, $[Ni(2,3-pyrazinedithiol)_2]$. *Inorg. Chem.* **2016**, *55* (4), 1433–1445.

(11) Kennedy, S. R.; Kozar, M. N.; Yennawar, H. P.; Lear, B. J. Steady-State Spectroscopic Analysis of Proton-Dependent Electron Transfer on Pyrazine-Appended Metal Dithiolenes $[Ni(pdt)_2]$, $[Pd(pdt)_2]$, and $[Pt(pdt)_2]$ (pdt = 2,3-Pyrazinedithiol). *Inorg. Chem.* **2016**, 55 (17), 8459–8467.

(12) Henfling, S.; Kempt, R.; Klose, J.; Kuc, A.; Kersting, B.; Krautscheid, H. Dithiol-Dithione Tautomerism of 2,3-Pyrazinedithiol in the Synthesis of Copper and Silver Coordination Compounds. *Inorg. Chem.* **2020**, *59* (22), 16441–16453.

(13) Basu, P.; Burgmayer, S. J. N. Recent developments in the study of molybdoenzyme models. *JBIC, J. Biol. Inorg. Chem.* **2015**, 20 (2), 373–383.

(14) Schulzke, C.; Ghosh, A. C. Molybdenum and Tungsten Oxidoreductase Models. In *Bioinspired Catalysis: Metal-Sulfur Complexes*; Weigand, W., Ed.; Wiley-VCH, 2014; pp 349–382. DOI: 10.1002/9783527664160.ch13.

(15) Kato, R.; Kobayashi, H.; Kobayashi, A.; Sasaki, Y. Crystal Structure of a new Molecular Conductor (DBTTF)[Ni(dmit) 2]. *Chem. Lett.* **1985**, *14* (1), 131–134.

(16) Olk, R.-M.; Kirmse, R.; Hoyer, E.; Faulmann, C.; Cassoux, P. Synthese und Eigenschaften von molekularen Leitern auf der Basis von dmit-isologen Chelaten Kristall- und Moleklstruktur des Tetramethylammonium-bis-[bis-(1,3-dithiol-2-selon-4,5-diselenolato)nickelat]; [(CH₃)₄N][Ni(dsise)₂]₂. Z. Anorg. Allg. Chem. **1994**, 620 (1), 90–100.

(17) Brossard, L.; Hurdequint, H.; Ribault, M.; Valade, L.; Legros, J. P.; Cassoux, P. Pressure-temperature phase diagram of α' -TTF [Pd(dmit)₂]₂. Synth. Met. **1988**, 27 (3-4), 157–162.

(18) Kobayashi, A.; Kobayashi, H.; Miyamoto, A.; Kato, R.; Clark, R. A.; Underhill, A. E. New Molecular Superconductor, β -[(CH₃)₄N]-[Pd(dmit)₂]₂. *Chem. Lett.* **1991**, 20 (12), 2163–2166.

(19) Kato, R.; Tajima, N.; Tamura, M.; Yamaura, J.-I. Uniaxial strain effect in a strongly correlated two-dimensional system $\beta' - (CH_3)_4$ As-[Pd(dmit)₂]₂. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2002**, *66* (2), 020508-1–020508-4.

(20) Kato, R. Conducting metal dithiolene complexes: structural and electronic properties. *Chem. Rev.* **2004**, *104* (11), 5319–5346.

(21) Weis, E. M.; Barnes, C. L.; Duval, P. B. $[Na_5(THF)_{10}Ce-(mnt)_4]_{\infty}$: a honeycomb network polymer that yields homoleptic

cerium(III) tetrakis(dithiolene) complexes in donor solvents. *Inorg. Chem.* **2006**, 45 (25), 10126–10130.

(22) Long, D.-L.; Cui, Y.; Chen, J.-T.; Cheng, W.-D.; Huang, J.-S. One-dimensional co-ordination polymers formed by crown ether metal cation bridges: synthesis and crystal structure of nickel(II) dithiolene complexes $[{Na(benzo-15-crown-5)}_2 Ni(i-mnt)_2]_n$. nCH_2Cl_2 and $[{Na(benzo-15-crown-5)}_2Ni(mnt)_2]_n$. Polyhedron 1998, 17 (22), 3969–3975.

(23) Baudron, S. A.; Hosseini, M. W. Sequential generation of onedimensional networks based on a differentiated bischelate-type ligand bearing both 4,5-diazafluorene and dithiolene units. *Inorg. Chem.* **2006**, 45 (14), 5260–5262.

(24) Ribas, X.; Dias, J. C.; Morgado, J.; Wurst, K.; Molins, E.; Ruiz, E.; Almeida, M.; Veciana, J.; Rovira, C. Novel Cu^{III} bis-1,2dichalcogenene complexes with tunable 3D framework through alkaline cation coordination: a structural and theoretical study. *Chem. - Eur. J.* **2004**, *10* (7), 1691–1704.

(25) Takaishi, S.; Hada, M.; Ishihara, N.; Breedlove, B. K.; Katoh, K.; Yamashita, M. Coordination mode-tuned stacking motif in alkali metal salts of Ni(pdt)₂ complexes (pdt = 2,3-pyrazinedithiol) and its physical properties. *Polyhedron* **2013**, *52*, 333–338.

(26) Bolligarla, R.; Das, S. K. Dimensionality of coordination polymers decided by the type of hybridization of the central carbon atom of the solvent molecule that coordinates to an alkali metal cation: from discrete to 3D networks based on a gold(III) bis(dithiolene) complex. *CrystEngComm* **2010**, *12* (11), 3409.

(27) Delgado, E.; Gómez-García, C. J.; Hernández, D.; Hernández, E.; Martín, A.; Zamora, F. Unprecedented layered coordination polymers of dithiolene group 10 metals: magnetic and electrical properties. *Dalton Trans.* **2016**, *45* (15), 6696–6701.

(28) Benmansour, S.; Delgado, E.; Gómez-García, C. J.; Hernández, D.; Hernández, E.; Martin, A.; Perles, J.; Zamora, F. Coordination polymers based on diiron tetrakis(dithiolato) bridged by alkali metals, electrical bistability around room temperature, and strong anti-ferromagnetic coupling. *Inorg. Chem.* **2015**, *54* (5), 2243–2252.

(29) Castillo, O.; Delgado, E.; Gómez-García, C. J.; Hernández, D.; Hernández, E.; Martín, A.; Martínez, J. I.; Zamora, F. Group 10 Metal Benzene-1,2-dithiolate Derivatives in the Synthesis of Coordination Polymers Containing Potassium Countercations. *Inorg. Chem.* **2017**, *56* (19), 11810–11818.

(30) Takaishi, S.; Hosoda, M.; Kajiwara, T.; Miyasaka, H.; Yamashita, M.; Nakanishi, Y.; Kitagawa, Y.; Yamaguchi, K.; Kobayashi, A.; Kitagawa, H. Electroconductive porous coordination polymer $Cu[Cu(pdt)_2]$ composed of donor and acceptor building units. *Inorg. Chem.* **2009**, *48* (19), 9048–9050.

(31) Kobayashi, Y.; Jacobs, B.; Allendorf, M. D.; Long, J. R. Conductivity, Doping, and Redox Chemistry of a Microporous Dithiolene-Based Metal–Organic Framework. *Chem. Mater.* **2010**, 22 (14), 4120–4122.

(32) Sun, L.; Campbell, M. G.; Dincă, M. Electrically Conductive Porous Metal-Organic Frameworks. *Angew. Chem., Int. Ed.* **2016**, 55 (11), 3566–3579.

(33) Bolligarla, R.; Durgaprasad, G.; Das, S. K. Synthesis, molecular structure and supramolecular chemistry of a new nickel-quinoxaline dithiolate system $[Bu_4N]_2[Ni(6,7\text{-}qdt)_2]$ (6,7-qdt = quinoxaline-6,7-dithiolate) and comparison of its electronic and electrochemical properties with those of $[Bu_4N]_2[Ni(qdt)_2]$ (qdt = quinoxaline-2,3-dithiolate). *Inorg. Chem. Commun.* **2011**, 14 (6), 809–813.

(34) Naik, I. K.; Sarkar, R.; Das, S. K. Bis(quinoxaline-dithiolato)nickel(III) Complexes $[Bu_4N][Ni^{III}(6,7\text{-}qdt)_2]$ and $[Ph_4P][Ni^{III}(Ph_2-6,7\text{-}qdt)_2]$ ·CHCl₃ (6,7-qdt = Quinoxaline-6,7-dithiolate; Ph₂-6,7-qdt = Diphenylquinoxaline-6,7-dithiolate): Synthesis, Spectroscopy, Electrochemistry, DFT Calculations, Crystal Structures and Hirshfeld Surface Analysis. *Eur. J. Inorg. Chem.* **2015**, 2015 (33), 5523–5533.

(35) Boyde, S.; Garner, C. D.; Clegg, W. A structural comparison of bis(quinoxaline-2,3-dithiolato)cuprate complexes. *J. Chem. Soc., Dalton Trans.* **1987**, *5*, 1083–1087.

(36) Dias, J. C.; Ribas, X.; Morgado, J.; Seiça, J.; Lopes, E. B.; Santos, I. C.; Henriques, R. T.; Almeida, M.; Wurst, K.; FouryLeylekian, P.; Canadell, E.; Vidal-Gancedo, J.; Veciana, J.; Rovira, C. Multistability in a family of DT–TTF organic radical based compounds $(DT-TTF)_4[M(L)_2]_3$ (M = Au, Cu; L = pds, pdt, bdt). J. Mater. Chem. 2005, 15 (31), 3187–3199.

(37) van der Bondi, A. Waals Volumes and Radii. J. Phys. Chem. 1964, 68 (3), 441-451.

(38) Bachler, V.; Olbrich, G.; Neese, F.; Wieghardt, K. Theoretical evidence for the singlet diradical character of square planar nickel complexes containing two *o*-semiquinonato type ligands. *Inorg. Chem.* **2002**, *41* (16), 4179–4193.

(39) Kokatam, S.; Ray, K.; Pap, J.; Bill, E.; Geiger, W. E.; LeSuer, R. J.; Rieger, P. H.; Weyhermüller, T.; Neese, F.; Wieghardt, K. Molecular and electronic structure of square-planar gold complexes containing two 1,2-Di(4-*tert*-butylphenyl)ethylene-1,2-dithiolato ligands: $[Au(^{2}L)_{2}]^{1+/0/1-/2}$. A combined experimental and computational study. *Inorg. Chem.* **2007**, *46* (4), 1100–1111.

(40) Lauterbach, C.; Fabian, J. Density Functional Derived Structures and Molecular Properties of Nickel Dithiolenes and Related Complexes. *Eur. J. Inorg. Chem.* **1999**, 1999 (11), 1995–2004.

(41) Bruno, G.; Almeida, M.; Artizzu, F.; Dias, J. C.; Mercuri, M. L.; Pilia, L.; Rovira, C.; Ribas, X.; Serpe, A.; Deplano, P. Innocence and noninnocence of the ligands in bis(pyrazine-2,3-dithiolate and -diselonate) d⁸-metal complexes. A theoretical and experimental study for the Cu(III), Au(III) and Ni(II) cases. *Dalton Trans.* **2010**, 39 (19), 4566–4574.

(42) Petrenko, T.; Ray, K.; Wieghardt, K. E.; Neese, F. Vibrational markers for the open-shell character of transition metal bisdithiolenes: an infrared, resonance raman, and quantum chemical study. *J. Am. Chem. Soc.* **2006**, *128* (13), 4422–4436.

(43) Kennedy, S. R.; Kozar, M. N.; Yennawar, H. P.; Lear, B. J. Synthesis and characterization of the gold dithiolene monoanion, $(Bu_4N)[Au(pdt = 2,3-pyrazinedithiol)_2]$. *Polyhedron* **2016**, *103*, 100–104.

(44) McCleverty, J. A. Metal 1,2-Dithiolene and Related Complexes. In *Progress in Inorganic Chemistry*; Cotton, F. A., Ed.; Interscience, 1968; Vol. 10, pp 49–221.

(45) Ševčík, A. Oscillographic polarography with periodical triangular voltage. *Collect. Czech. Chem. Commun.* 1948, 13, 349–377.
(46) Randles, J. E. B. A cathode ray polarograph. Part II.—The

current-voltage curves. Trans. Faraday Soc. **1948**, 44 (0), 327–338. (47) Hamann, C. H.; Vielstich, W. Elektrochemie, 4., vollständig überarbeitete und aktualisierte Auflage; Wiley-VCH-Verlag GmbJ & Co., KGaA, 2005.

(48) Hayashi, M.; Otsubo, K.; Kato, T.; Sugimoto, K.; Fujiwara, A.; Kitagawa, H. A compact planar low-energy-gap molecule with a donor-acceptor-donor nature based on a bimetal dithiolene complex. *Chem. Commun.* **2015**, *51* (87), 15796–15799.

(49) Tommasino, J.-B.; Pomarede, B.; Medus, d.; de Montauzon, D.; Cassoux, P.; Fabre, P.-L. Electrochemical Studies of the Formation Mechanism of $(cation)_x[Ni(dmit)_2]$ Conductive Compounds and of their Non-Integer Oxidation State. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1993**, 237 (1), 445–456.

(50) Pullen, A. E.; Olk, R.-M.; Zeltner, S.; Hoyer, E.; Abboud, K. A.; Reynolds, J. R. A New Generation of Nickel-dmit-Based Molecular Conductors Based on Fully Conjugated Bimetallic Complexes. *Inorg. Chem.* **1997**, *36* (6), 958–959.

(51) Bereman, R. D.; Lu, H. Synthesis and characterization of the nickel and copper complexes of the new dithiolene, 1,3-propanediyldithioethylene-1,2-dithiolate (PDDT). *Inorg. Chim. Acta* **1993**, 204 (1), 53–61.

(52) Curreli, S.; Deplano, P.; Faulmann, C.; Ienco, A.; Mealli, C.; Mercuri, M. L.; Pilia, L.; Pintus, G.; Serpe, A.; Trogu, E. F. Electronic factors affecting second-order NLO properties: case study of four different push-pull bis-dithiolene nickel complexes. *Inorg. Chem.* **2004**, 43 (16), 5069–5079.

(53) Beswick, C. L. Synthesis of Transition Metal Dithiolenes in Dithiolene Chemistry. In *Dithiolene Chemistry*; Stiefel, E. I., Ed.; John Wiley & Sons, Inc, 2003; pp 55–110.

(54) Stamp, L.; Tom Dieck, H. Copper(I) complexes with unsaturated nitrogen ligands. Part IV. Synthesis and structure of copper(I) monoazadiene complexes. *Inorg. Chim. Acta* **1988**, *147* (2), 199–206.

(55) Balamurugan, R.; Palaniandavar, M.; Gopalan, R. S. Trigonal planar copper(I) complex: synthesis, structure, and spectra of a redox pair of novel copper(II/I) complexes of tridentate bis(benzimidazol-2'-yl) ligand framework as models for electron-transfer copper proteins. *Inorg. Chem.* **2001**, *40* (10), 2246–2255.

(56) Dance, I. G.; Bowmaker, G. A.; Clark, G. R.; Seadon, J. K. The formation and crystal and molecular structures of hexa(μ -organothiolato)tetracuprate(I) cage dianions: bis-(tetramethylammonium)hexa-(μ -methanethiolato)tetracuprate(I) and two polymorphs of bis(tetramethylammonium)hexa-(μ -benzenethiolato)-tetracuprate(I). *Polyhedron* **1983**, 2 (10), 1031–1043.

(57) Konno, T.; Okamoto, K.; Hidaka, J. Synthesis and structure of unprecedented copper(I)-rhodium(III) $\text{Cu}_4^{\text{I}}\text{Rh}_4^{\text{III}}$ and copper(I)-iridium(III) $\text{Cu}_4^{\text{I}}\text{I}\text{rh}_4^{\text{III}}$ S-bridged polynuclear complexes containing μ_2 - and μ_3 -thiolato and coordinated disulfide: spontaneous reduction of copper(II) to trigonal-planar copper(I). *Inorg. Chem.* **1992**, *31* (19), 3875–3876.

(58) Knotter, D. M.; van Maanen, H. L.; Grove, D. M.; Spek, A. L.; van Koten, G. Synthesis and properties of trimeric ortho-chelated (arenethiolato)copper(I) complexes. *Inorg. Chem.* **1991**, *30* (17), 3309–3317.

(59) Baumgartner, M.; Schmalle, H.; Dubler, E. Synthesis, characterization and crystal structure of copper(I) thiolates: $[(C_6H_5)_4P^+]_2[Cu_4(C_2H_5S^-)_6] \cdot 0.5C_2H_6O_2$ and $[(C_6H_5)_4P^+]_2[Cu_7(C_2H_5S^-)_8]$. Polyhedron **1990**, 9 (9), 1155–1164.

(60) Nicholson, J. R.; Abrahams, I. L.; Clegg, W.; Garner, C. D. Preparation, crystal structure, and spectroscopic characterization of the tetranuclear copper-thiolate cluster $[Cu_4(o-(SCH_2)_2C_6H_4)_3]^{2-}$ as its tetraphenylphosphonium(1+) salt. *Inorg. Chem.* **1985**, 24 (7), 1092–1096.

(61) Liu, C. W.; Stubbs, T.; Staples, R. J.; Fackler, J. P. Syntheses and Structural Characterizations of Two New Cu-S Clusters of Dialkyl Dithiophosphates: A Sulfide-Centered CuI₈ Cube, { $Cu_8[S_2P-(OiP_1)_2]_6(\mu_8-S)$ }, and a Distorted Octahedral { $Cu_6[S_2P(OEt)_2]_6$. 2H₂O} Cluster. J. Am. Chem. Soc. **1995**, 117 (38), 9778–9779.

(62) Gennari, M.; Pécaut, J.; DeBeer, S.; Neese, F.; Collomb, M.-N.; Duboc, C. A Fully Delocalized Mixed-Valence Bis- μ (Thiolato) Dicopper Complex: A Structural and Functional Model of the Biological Cu_A Center. *Angew. Chem.* **2011**, *123* (25), 5780–5784.

(63) Houser, R. P.; Young, V. G.; Tolman, W. B. A Thiolate-Bridged, Fully Delocalized Mixed-Valence Dicopper(I,II) Complex That Models the Cu_A Biological Electron-Transfer Site. J. Am. Chem. Soc. **1996**, 118 (8), 2101–2102.

(64) Stibrany, R. T.; Fikar, R.; Brader, M.; Potenza, M. N.; Potenza, J. A.; Schugar, H. J. Charge-transfer spectra of structurally characterized mixed-valence thiolate-bridged Cu(I)/Cu(II) cluster complexes. *Inorg. Chem.* **2002**, *41* (20), 5203–5215.

(65) Josien, M.-L.; Fuson, N. Infrared Study of the Effect of Solvent upon ν (NH) in Pyrrole. J. Chem. Phys. **1954**, 22 (7), 1169–1177.

(66) Rao, C. N. R.; Venkataraghavan, R. Contribution to the Infrared Spectra of Five-Membered N- and N,S- Heterocyclic Compounds. *Can. J. Chem.* **1964**, *42* (1), 43–49.

(67) Hathaway, B. J.; Billing, D. E. The electronic properties and stereochemistry of mono-nuclear complexes of the copper(II) ion. *Coord. Chem. Rev.* **1970**, 5 (2), 143–207.

(68) Jiang, Y.; Huang, J.; Kasumaj, B.; Jeschke, G.; Hunger, M.; Mallat, T.; Baiker, A. Adsorption-desorption induced structural changes of Cu-MOF evidenced by solid state NMR and EPR spectroscopy. J. Am. Chem. Soc. **2009**, 131 (6), 2058–2059.

(69) Kirmse, R.; Strauch, P. EPR-Untersuchungen an Kupfer(II)-Bis-Komplexen mit Thiooxalaten. *Z. Anorg. Allg. Chem.* **1991**, 600 (1), 61–66.

(70) Peisach, J.; Blumberg, W. E. Structural implications derived from the analysis of electron paramagnetic resonance spectra of

natural and artificial copper proteins. Arch. Biochem. Biophys. 1974, 165 (2), 691-708.

(71) Bonner, J. C.; Fisher, M. E. Linear Magnetic Chains with Anisotropic Coupling. *Phys. Rev.* **1964**, *135* (3A), A640–A658.

(72) Hatfield, W. E.; Weller, R. R.; Hall, J. W. Exchange coupling in the sulfur-bridged quasi-linear-chain compound bis-(dimethyldithiocarbamato)copper(II). Observations on exchange in sulfur-bridged copper(II) compounds. *Inorg. Chem.* **1980**, *19* (12), 3825–3828.