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A mixed valence zinc dithiolene system with spectator metal and reactor ligands

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Abstract

Neutral complexes of zinc with N,N'-diisopropylpiperazine-2,3-dithione (iPr_2Dt^0) and N,N'-dimethylpiperazine-2,3-dithione (Me_2Dt^0) with chloride or maleonitriledithiolate (mnt^{2-}) as coligands have been synthesized and characterized. The molecular structures of these zinc complexes have been determined using single crystal X-ray diffractometry. Complexes recrystallize in monoclinic P type systems with zinc adopting a distorted tetrahedral geometry. Two zinc complexes with mixed-valent dithiolene ligands exhibit ligand-to-ligand charge transfer bands. Optimized geometries, molecular vibrations and electronic structures of charge-transfer complexes were calculated using density functional theory (B3LYP/6-311G+(d,p) level). Redox orbitals are shown to be almost exclusively ligand in nature, with a HOMO based heavily on the electron-rich maleonitriledithiolate ligand, and a LUMO comprised mostly of the electron-deficient dithione ligand. Charge transfer is thus believed to proceed from dithiolate HOMO to dithione LUMO, showing ligand-to-ligand redox interplay across a d^{10} metal.

Graphical Abstract

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Supporting Information. Crystallographic information files, atomic coordinates of DFT optimized molecular geometries in z-matrix format, schematic diagrams of complexes used for τ_4 and τ_8 comparison, and a list of τ_4 and τ_8 values for reported zinc dithiolene complexes available in the CSD.

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Introduction

Understanding how a redox-active ligand can interact with a transition metal ion is a fundamental theme in coordination chemistry that has significant implications in materials and biological sciences. Among the many redox-active ligands, ene-1,2-dithiolate, or dithiolene ligands, are considered to be prototypical examples of redox-non-innocent ligands.[1, 2] As shown in Scheme 1, the dithiolene unit is able to reversibly shuttle between a fully reduced (dithiolate) and a fully oxidized (dithione) form via a two-electron oxidation/reduction without altering the formal redox state of the metal.[3] The coordination chemistry of the reduced dithiolene ligand has been explored since the early 1960s, and still provides new insight into metal-ligand interactions.[4] Zinc dithiolene complexes have been studied as possible conductive, magnetic, and functional polymer materials.[5–7] Mixed-donor dithiolene ligand complexes have also been shown to exhibit luminescence due to a ligand-to-ligand charge transfer process.[8] The vast majority of dithiolenes studied assume the fully reduced dithiolate state; conversely, the fully-oxidized dithione state has been largely overlooked. Despite being understudied, complexes of fully oxidized dithiolene ligands (i.e. dithione) have been shown to aid in noble metal recovery, as well as exhibit non-linear optical properties.[9–12]

While much work has gone into the development of complexes with redox-active metals, the coordination chemistry of dithiolene with a closed-shell d -block metal (e.g. zinc) remains largely unexplored; [5–8, 13–19] this is not surprising as the objective has been to

understand the electronic partition between the redox active ligands and a redox active metal. Recently, it has become increasingly clear that redox active metals may function as a spectator anchoring point for interaction between two redox active ligands.[20] To this end, we have been engaged in studying metal-ligand interactions using a dithione ligand, i.e., the fully oxidized π -accepting ligand using a redox-active metal.[20, 21] In the case presented, an electron rich π -donating dithiolate ligand is added alongside a dithione ligand, and a molecular system with built-in electron rich and electron deficient moieties can be created, a situation made possible by the redox versatility of the dithione ligand. Because of the presence of potential ligand to ligand charge transfer (LLCT) transitions, these electronic donor-acceptor systems are of great interest as materials for information storage and switching.[22]

Recently, we have reported a four coordinate square planar d^8 Ni(II) mixed valence ligand system that exhibit low energy LLCT band, where the metal center acts as an anchoring point for ligand coordination.[20] Herein we report another four coordinate metal system where the two dithiolene ligands are in varying redox states. An inherently redox inactive d^{10} Zn(II) ion serves as the metal center in the present case. We report the design, synthesis, and characterization of the molecules shown in Figure 1. We also report the electronic structures of the two mixed valence complexes **3** and **4** as understood by density functional theory (DFT) calculations. The three dimensional molecular structures of all complexes presented in Figure 1 have been determined by X-ray crystallography.

Results

Synthesis and Characterization

The mono-dithione chloride complexes **1** and **2** were synthesized by addition of the respective dithione ligand to a suspension of ZnCl_2 in acetonitrile. The target compounds **1** and **2** were isolated as crystalline yellow solids from an acetonitrile solution layered with ether. In the solid state both complexes were stable in air. These chloride complexes were readily soluble in moderately polar solvents such as acetonitrile and DMF to yield yellow solutions. Acetonitrile solutions of the complexes were stable in air. Complexes **3** and **4** were synthesized via exchange of the chloride ligands for maleonitriledithiolate. The smooth ligand exchange reaction is presumably driven by the chelate effect of the dithiolene moiety. Thus, addition of Na_2mnt to a methanolic suspension of **1** and **2** affords compounds **3** and **4**, respectively. Due to their relative insolubility in methanol, **3** and **4** precipitated from the solution upon substitution of the chloride ligands for maleonitriledithiolate. Both **3** and **4** are freely soluble in acetonitrile, sparingly soluble in methanol and insoluble in chloroform and dichloromethane.

Solid-state FT-IR spectra were collected from the crystalline solids. The $\nu(\text{C}=\text{S})$ vibration shifts from 1462 cm^{-1} in uncoordinated Pr_2Dt^0 ligand to 1504 cm^{-1} and 1501 cm^{-1} in **1** and **3**, respectively. The $\nu(\text{C}=\text{S})$ vibration shifts from 1501 cm^{-1} in unbound Me_2Dt^0 ligand to 1531 cm^{-1} and 1533 cm^{-1} in **2** and **4**, respectively. In both ligands the $\nu(\text{C}=\text{S})$ vibrational frequency is increased ($\sim 40\text{ cm}^{-1}$ and 30 cm^{-1} for Pr_2Dt^0 and Me_2Dt^0 , respectively) upon coordination to Zn. However, this frequency does not increase when two chloride ligands are

replaced with the maleonitriledithiolate ligand. A similar trend is also observed in the $\nu((\text{N}-\text{C})=\text{S})$ coupled vibration. In uncoordinated Pr_2Dt^0 ligand, the $\nu((\text{N}-\text{C})=\text{S})$ vibration is observed at 1343 cm^{-1} which shift to 1363 cm^{-1} and 1365 cm^{-1} , respectively for **1** and **3**. For the uncoordinated Me_2Dt^0 this band appears at 1335 cm^{-1} , which shifts to 1361 cm^{-1} and 1368 cm^{-1} , respectively for **2** and **4**. We attribute this shift to the higher energy to the $\text{C}(\text{N})-\text{C}(\text{S})-\text{C}(\text{S})-\text{C}(\text{N})$ fragment of the dithione ligand being conformationally more rigid and planar due to the coordination to Zn. This feature is further explored in the discussion of molecular structures. In both **3** and **4** the maleonitriledithiolate ligand exhibits $\nu(\text{C}-\text{S})$ and $\nu(\text{C}\equiv\text{N})$ vibrations at 858 cm^{-1} and $\sim 2195\text{ cm}^{-1}$. The $\nu(\text{C}-\text{S})$ and $\nu(\text{C}\equiv\text{N})$ vibrations in the maleonitriledithiolate sodium salt are observed at 857 cm^{-1} and 2192 cm^{-1} , respectively.

The room temperature ^1H NMR spectra of the complexes are very similar to those of the corresponding unbound dithione ligands. For example, uncoordinated Pr_2Dt^0 ligand exhibits three resonances at δ 5.39 (CH), δ 3.43 (CH_2), and δ 1.24 (CH_3). These resonances shift only marginally; the CH protons resonate at δ 5.24 and δ 5.22, respectively for **1** and **3**, whereas CH_3 groups resonate at δ 1.35 and δ 1.37, respectively, while the methylene protons resonate at δ 3.73 and δ 3.76, respectively for **1** and **3**. Thus, the largest shift is observed for the ring methylene protons. Uncoordinated Me_2Dt^0 ligand protons exhibit two singlet peaks at δ 3.57 and δ 3.74 for CH_3 and CH_2 protons, respectively. Complexes of Me_2Dt^0 ligand i.e., **2** and **4** exhibit identical resonance patterns with singlet peaks at δ 3.64 and δ 3.66 for methyl and methylene protons, respectively.

Electronic Spectra

Room temperature electronic spectra of acetonitrile solutions of **1**, **2**, **3**, and **4** are shown in Figure 2. Compounds **1** and **2** exhibit two strong bands at 315 nm and 224 nm. In addition, a shoulder at $\sim 415\text{ nm}$ is observed for both complexes. The 315 nm band shifts to 259 nm in **3** and **4**, and the bands at 216 nm and 224 nm shift to 205 nm and 208 nm in **3** and **4**, respectively. Coordination of the reduced dithiolene ligand gives rise to a strong third band observed at 360 nm in both **3** and **4**. In addition, these two complexes exhibit a broad low-energy band at 480 nm ($\sim 480\text{ M}^{-1}\text{cm}^{-1}$) and 490 nm ($\sim 150\text{ M}^{-1}\text{cm}^{-1}$) for **3** and **4**, respectively. Based on the extinction coefficient and the d^{10} configuration of the metal center, these bands are assigned as charge transfer in origin between the two dithiolene ligands of differing redox states.

Molecular Structure Description

Molecular structures for **1**, **2**, **3**, and **4** were determined using single crystal X-ray diffraction and are shown in Figure 3. General crystallographic information is given in Table 1, and selected bond lengths and angles are given in Table 2.

Molecular structures of **1** and **2** both exhibit a distorted tetrahedral Zn metal center. As expected, the fully oxidized character of the dithione ligand is retained upon coordination to the Zn center. The $\text{Zn}-\text{S}$ distances are $\sim 2.35\text{ \AA}$, slightly longer than the $\text{Zn}-\text{Cl}$ distance of $\sim 2.22\text{ \AA}$. The $\text{C}=\text{S}$ distances are slightly shorter than what is expected for a $\text{C}-\text{S}$ single bond distance. In both complexes, the $\text{C}(\text{S})-\text{C}(\text{S})$ distance however, is $\sim 1.5\text{ \AA}$, typical for a $\text{C}-\text{C}$ single bond suggesting dithione ligand character. Complex **1** exhibits a $\text{S}-\text{C}-\text{C}-\text{S}$

torsion of 31.1(2)°, while the same torsion is observed as 19(1)° in **2**. Uncoordinated ligand S-C-C-S torsions are -36.9(6)° for Pr_2Dt^0 and -36.6(5)° for Me_2Dt^0 ligands (values obtained from Cambridge Crystallographic Data Center (CCDC) structure codes KAYZUF and RUPHAM, respectively for Pr_2Dt^0 and Me_2Dt^0).

The zinc metal center in **3** and **4** assumes a distorted tetrahedral geometry. In **3** an acetonitrile molecule was also found in the crystal lattice. In **3** and **4**, Zn is coordinated by two dithiolene ligands of different oxidation states, providing an opportunity for direct comparison in the same molecular frame. Zn-S(dithione) bonds are marginally elongated ~0.05 Å as compared to Zn-S (dithiolate) bonds suggesting that the two types of Zn—S bonds are essentially similar. In **3**, dithione Zn-S bonds are asymmetrical with a difference of ~0.03 Å. A decrease of ~0.025 Å is observed in dithione Zn-S bonds between **2** and **4**. C=S bond distances for the dithione ligand in **3** (1.66(5) Å, 1.681(1) Å) and **4** (1.682(1) Å, 1.683(1) Å) are almost identical to those observed in **1** and **2**. The maleonitriledithiolate C-S bond distances are considerably shorter (1.731(5) Å, 1.740(6) Å), indicating a clear difference in ligand oxidation states. Ligand mixed-valency is further evidenced by short (~1.35 Å) maleonitriledithiolate C1-C2 bonds that are indicative of double bond-character. Conversely, dithione C5-C6 bonds in both **3** and **4** are ~1.5 Å in length, exhibiting clear single bond character. Thioamide (S=(C-N)) bond distances for **3** and **4** are observed at ~1.31 Å. Dithione unit torsions (S3-C5-C6-S4) were found to be 19.9(5)° in **3**, and -24.6(2)° in **4**; dithiolate unit torsions (S1-C1-C2-S2) were observed to be -0.8(7)° and -0.1(2)° in **3** and **4**, respectively. The planarity of the dithiolate mnt^{2-} ligand relative to the distorted dithione ligands seen in both **3** and **4** provides further evidence of isolated ligand redox character. In **3**, the dithione ligand backbone twists out of the chelate plane by of 21.99° (angle between the planes containing S3, Zn1, S4, and S3, C5, C6, S4). This degree of distortion is not observed in **4**, which exhibits nearly coplanar dithione and chelation planes.

Computational analysis

Geometry optimizations for **3** and **4** at the B3LYP/6-311G+(d, p) level of theory predict a tetrahedral zinc coordination. Vibrational frequency calculations obtained from the same level of theory have been compared to the solid-state IR for **4** (Figure 4). Unscaled vibrational frequencies generated by DFT for both **3** and **4** closely predict the relative peak locations observed in the solid state FTIR spectra. In particular, predicted frequencies for the diagnostic ν (C=S) and ν (C-N) vibrations deviate by 8 cm^{-1} and 12 cm^{-1} , respectively, in **3** and 7 cm^{-1} and 2 cm^{-1} , respectively, in **4**.

The DFT calculated molecular orbital diagrams for **3** are shown in Figure 5. The frontier orbitals for both **3** and **4** are predominantly ligand-based. The HOMO and LUMO are isolated from nearby orbitals, as both the HOMO-1 and LUMO+1 exhibit a considerable difference in energy from their respective closest orbitals. The HOMO-1,-2 and LUMO +1,+2 pairs are close in energy, leading to clustered orbitals both above and below the HOMO/LUMO pair. Molecular orbital compositions of **3** and **4** were calculated using C-squared population analysis and the resulting compositions are tabulated in Table 3. Frontier orbitals of **3** and **4** were found to be primarily ligand based. In **3** the HOMO is observed to be predominantly dithiolate in character (~42%) and the LUMO was found to originate

mostly from the dithione unit (~57%). Both LUMO and HOMO are localized primarily on the S atoms. In **4**, however, the ligand contributions to the HOMO and LUMO are less discrete. The HOMO of **4** is ~47% dithiolate and ~41% dithione character, and the LUMO is ~37% dithiolate and 35% dithione character. In both **3** and **4**, Zn makes negligible contribution to the frontier orbitals. The HOMO and LUMO are energetically well separated; for **3** the separation is 1.16 eV and for **4** it is 1.01 eV.

Discussion

Four dithione-Zn complexes have been synthesized and characterized. In two complexes, Zn is coordinated by one dithione and one dithiolene ligands. Molecular structures of all complexes have been determined by X-ray crystallography. Having dithiolenes of opposite oxidation states within the same molecule provides the opportunity to compare critical ligand bond lengths based on the ligand oxidation state. The ~0.14 Å elongation of dithiolate C-S bonds compared to dithione C-S bonds in **3** and **4** suggests that the dithiolene ligands exhibit distinct oxidation states. Almost identical dithione C=S bond lengths of ~1.68 Å were observed in **1-4**. Complex **1** was found to exhibit a dithione (S-C-C-S) torsion (31.1(2)°) higher than that observed in **2** (19(1)°). Similarly, complex **3** exhibits a great deal of distortion of the Pr_2Dt^0 ligand. The observed distortion in **3** could be either electronic or steric in origin. In **1** and **3**, the larger isopropyl groups lead to distortions in the chelate ring.

Distortion observed in the solid-state molecular structures was quantified using the τ_4 and τ_8 distortion indices. Since the introduction of the τ index by Addison and coworkers to determine the degree of distortion about five-coordinate system, there have been several proposed indices that adapt this concept to four-coordinate systems.[23–26] We utilize one such index developed by Yang *et al.*, τ_4 , that quantifies four-coordinate distortion with the following equation: $\tau_4 = \frac{360^\circ - (\alpha + \beta)}{141^\circ}$ where α and β are the two largest bond angles about the metal center.[24] In this system a perfect square planar geometry gives $\tau_4 = 0$ while a tetrahedral geometry gives $\tau_4 = 1$; intermediate geometries lie on a continuum between these two values. Recently, Kubiak and coworkers have proposed an amended version of this index, $\tau_\delta = \frac{360^\circ - (\alpha + \beta)}{141^\circ} \delta$, where $\delta = \frac{\beta}{\alpha}$. The inclusion of the δ term is intended to aid in distinguishing between “true” sawhorse geometries and complexes that exhibit tetrahedral geometries severely distorted by their ligand environment. Values of τ_δ can be interpreted on the same scale as τ_4 . [23] Table 4 gives τ_4 and τ_δ values for **1-4**, as well as for several reported dithiolene ligand complexes. Structures were chosen from the 48 reported four-coordinate zinc dithiolene complexes available in the CSD. Many of the structures are cationic substitutions of the same zinc-containing anion; structures chosen for calculations aim to represent each type of reported zinc dithiolene complex. All reported complexes except $\text{Zn}(\text{mnt})(4\text{-Me-Py})$ and $\text{Zn}(\text{H}_2\text{dmdto})\text{Cl}_2$ are chelated by two bidentate ligands, causing significant strain on the tetrahedral center. The τ_4 and τ_δ values for these complexes are all less than 0.8, whereas the four lowest τ values belong to complexes (**1**, **2**, $\text{Zn}(\text{mnt})(4\text{-Me-Py})_2$, and $\text{ZnCl}_2(\text{H}_2\text{dmdto})$ bound by a single bidentate and two monodentate ligands. The more relaxed arrangement causes less strain on the optimal tetrahedral geometry, which is reflected in the lower τ_4 and τ_δ values. Generally, the two indices agree on the degree of distortion in the selected complexes. This is not surprising, as differences in the two indices

should be observed in ligands that force a high degree of distortion on the metal center. Of the compounds described in this work, complex **3** exhibits the lowest τ_4 and τ_8 values, indicating a high degree of distortion; **3** also has one of the highest degrees of distortion as compared to the 48 literature zinc dithiolene structures (full list of τ_4 and τ_8 values for these complexes available in Table S3 of the supporting information). Complexes with higher degrees of distortion (and thus smaller τ_4 and τ_8 values) are primarily bis-complexes of either maleonitriledithiolate or dmit (2-thioxo-1,3-dithiol-4,5-dithiolato). This distortion of **3** may be due to the solvent acetonitrile molecule sterically interacting with the piperazine dithione ring, leading to greater potential distortion of the metal center geometry. Alternatively, the distortion could be electronic in origin at least in part. The electronic distortion is also manifested in the LLCT transition with a higher extinction coefficient. Unlike in $\text{Zn}(\text{mnt})(4\text{-Me-Py})$ and $\text{Zn}(\text{H}_2\text{dmdto})\text{Cl}_2$ where distinct inter-molecular interaction are observed, the packing of **3** does not show any strong interaction with the solvent it seems likely that the electronic factor may be more dominant in the present case.

The electronic structures of **3** and **4** were calculated using density function theory; calculations indicate that both HOMO and LUMO orbitals are almost strictly ligand based. The zinc center makes little contribution to frontier orbitals, as is expected of a d^{10} metal. In **3**, the HOMO is primarily dithiolate in character while the LUMO is heavily dithione in character. This orbital partitioning suggests that ligand-to-ligand charge-transfer proceeds from dithiolate ligand to dithione ligand, as has been previously documented in redox-active metal systems.[11] In **4**, however, the dithiolate and dithione ligands make almost equal contribution to the HOMO and LUMO frontier orbitals. This disparity in MO composition between **3** and **4** would explain the electronic spectrum observations. Both **3** and **4** exhibit lower-intensity bands attributable to ligand-to-ligand charge transfer at 480 nm and 490 nm, respectively, with **3** having a higher intensity transition than **4**. The MO composition in **3** could explain its greater transition intensity, as electron density is concentrated on the maleonitriledithiolate ligand while the dithione ligand remains electron deficient. This electronic description suggests a donor-acceptor system that supports the hypothesized ligand-to-ligand charge transfer.

Conclusion

Dithiolene ligands continue to be an intriguing area of chemical research due their ability to exist in either a fully oxidized (dithione) or fully reduced state (dithiolate). In this study, we examined mixed-valence dithiolene ligand complexes about the non-redox active $\text{Zn}(\text{II})$ metal center in order to probe potential ligand-to-ligand interactions. Complexes **3** and **4** exhibit low-energy ligand-to-ligand charge transfer bands at ~480 nm. Solid-state molecular structures for complexes **1**, **2**, **3**, and **4** were determined using X-ray crystallography. Structures of **3** and **4** indicate that both dithiolene ligands retain their original oxidation states upon coordination to the metal center. Distortion of tetrahedral zinc geometry was quantified using τ values. The τ values of **1-4** were given alongside those of several literature zinc dithiolene complexes obtained from the CCDC. The molecular structure of **3** exhibited the most distorted tetrahedral center of the molecules reported in this work, as determined by calculation of τ_4 and τ_8 distortion indices. The electronic structures of **3** and

4 were calculated using DFT. Calculated HOMOs and LUMOs were found to be predominantly ligand in origin, with the HOMO based in the dithiolate moiety of the maleonitriledithiolate ligand and LUMO based in the dithione ligand in **3**. MO structures suggest ligand-to-ligand charge transfer involves electron flow from dithiolate to dithione ligands.

Experimental

Solvents were purchased from commercial sources such as the Aldrich Chemical Co. and the Acros Chemical Co. and were deoxygenated using the freeze-pump-thaw technique, and were stored in a drybox until use. Reagents were purchased from commercial sources such as Acros Chemical Co., and were de-gassed before use. The $^i\text{Pr}_2\text{Dt}^0$ and Me_2Dt^0 ligands were synthesized according to literature procedure.[27] UV-visible spectra were recorded on a Cary 100 spectrometer. ^1H and ^{13}C NMR spectra were collected using either a Bruker AVANCE 400 or 500 MHz NMR spectrometer. IR Spectra were collected neat using a Thermo Nicolet 380 FT-IR spectrometer. Elemental analysis was performed by Midwest Microlab LLC, Indiana, IL. X-ray quality crystals of **1** were obtained via vapor diffusion of hexanes into a concentrated acetonitrile solution. Crystalline product of **2** was used directly for X-ray diffraction studies. Crystals of **3** and **4** were grown using slow vapor diffusion of ether into a concentrated acetonitrile solution. X-ray crystallography data was collected using a Bruker APEX2 X-ray diffractometer using graphite-monochromatized Mo- K_α radiation ($\lambda = 0.71073$) at room temperature. Crystal structures of **1-4** were solved using direct methods. Structure refinements were performed using SHELXL2013 software accompanied by the ShelXle GUI.[28] Crystals were harvested, mounted on a glass fiber using super glue, and coated in paratone oil.

Computational Details

DFT calculations were performed using Gaussian 09.[29] Molecular orbital compositions were calculated via C-squared population analysis using QMForge software. [30] Initial optimizations of complexes were performed at the B3LYP/6-31G level of theory with geometries in which ligands were arranged randomly around a Zn(II) center with dithiolene units facing the metal. The subsequent minima identified after initial calculations were used for full optimization and vibrational frequency calculations at the B3LYP/6-311G+(d,p) level of theory for all atoms. This level of theory was chosen due to its well documented ability to model metal dithiolenes.[20, 21] The vibrational frequency calculations were performed to (a) confirm that structures were true minima and (b) to aid in the assignment of molecular vibrational modes. The calculated infrared spectrum for **4** is presented in Figure 4. Our intent was not to match the solid-state infrared spectrum, but rather to identify sample-specific vibrations. Therefore, no attempt was made to convert the calculated spectrum to absorbance or transmittance. The DFT calculations also allowed us to ascertain the general composition of redox orbitals. Our intent was not to conduct an extensive investigation into the electronic structure of **3** and **4**, so orbital energies are taken as relative.

Synthesis of ZnCl_2 ($^i\text{Pr}_2\text{Dt}^0$) (1)

In a 100 mL Schlenk flask 0.15 g (1.10 mmol) of ZnCl_2 was dissolved in 10 mL of acetonitrile and stirred for 10 min. To this solution, 0.25 g (1.09 mmol) of $^i\text{Pr}_2\text{Dt}^0$ was added. The reaction mixture was then allowed to stir for 30 min and then filtered to obtain pure product. The precipitate was rinsed with CH_2Cl_2 to remove excess $^i\text{Pr}_2\text{Dt}^0$. The yield was 0.30 g (0.82 mmol, 75%).

Characterization—Anal. Calcd. (experimental) for $\text{ZnC}_{10}\text{H}_{18}\text{Cl}_2\text{N}_2\text{S}_2$: C, 32.76 (33.04); H 4.95 (4.88); N 7.64 (7.49), ^1H NMR (^1H , δ , ppm) in Acetonitrile: 5.24 (p, 2H, CH, $J = 6.6$ Hz), 3.73 (s, 4H, CH_2), 1.35 (d, 6H, CH_3 , $J = 6.6$ Hz). IR (cm^{-1}): 1364 (m, C=S), 1504 (s, C-N).

Synthesis of ZnCl_2 (Me_2Dt^0) (2)

In a 100 mL Schlenk flask 0.050 g (0.38 mmol) of ZnCl_2 was dissolved in ~ 10 mL of acetonitrile. 0.082 g, (0.46 mmol) of Me_2Dt^0 was then added to the solution, which was then stirred for 30 min. The reaction mixture was then layered with diethyl ether and set to recrystallize at ambient temperature. Crystalline product was filtered and rinsed with ~10 mL of cold (-4°C) CHCl_3 . The yield was 0.054 g (0.17 mmol, 47%).

Characterization—Anal. Calcd. (experimental) for $\text{ZnC}_6\text{H}_{10}\text{Cl}_2\text{N}_2\text{S}_2$: C, 23.21 (23.60); H 3.25 (3.22); N 9.02 (8.82), ^1H NMR (^1H , δ , ppm) in Acetonitrile: 3.94 (s, 6H, CH_3), 3.66 (s, 4H, CH_2). IR (cm^{-1}): 1361 (s, C=S), 1537 (s, C-N).

Synthesis of $\text{Zn}(\text{mnt})(^i\text{Pr}_2\text{Dt}^0)$ (3)

In a 100 mL Schlenk flask ZnCl_2 (0.100 g, 0.734 mmol) was dissolved in 10 mL of MeOH and $^i\text{Pr}_2\text{Dt}^0$ (0.169 g, 0.734 mmol) was added neat. The mixture was stirred for 1 hr., yielding a yellow solution with a fine yellow precipitate. Na_2mnt (0.137 g, 0.734 mmol) was then added neat and the mixture was stirred for 3 hrs, yielding a red-orange solution with a fine orange precipitate. The solution was layered with 20 mL Et_2O and allowed to sit overnight. The solution was then filtered, giving a deep red powder that was washed with 5 X 1 mL EtOH to give a dark red $\text{Zn}(\text{mnt})(^i\text{Pr}_2\text{Dt}^0)$ (0.2892 g, 0.6634 mmol, 90%).

Characterization—Anal. Calcd. (experimental) for $\text{ZnC}_{14}\text{H}_{18}\text{N}_4\text{S}_4 \cdot 0.5\text{NaCl}$: C, 36.14 (36.78); H 3.90 (3.99); N 12.04 (11.81), ^1H NMR (^1H , δ , ppm) in Acetonitrile: 5.22 (p, CH, 2H, $J = 6.7$ Hz), 3.76 (s, 4H, CH_2), 1.37 (d, CH_3 , 12H $J = 6.3$ Hz). IR (cm^{-1}): 859 (m, C-S), 1365 (m, C=S), 1500.7 (s, C-N), 2194 (s, $\text{C}\equiv\text{N}$).

Synthesis of $\text{Zn}(\text{mnt})(\text{Me}_2\text{Dt}^0)$ (4)

In a 100 mL Schlenk flask ZnCl_2 (0.101 g, 0.741 mmol) was dissolved in 10 mL of MeOH and Me_2Dt^0 (0.129 g, 0.734 mmol) was added neat. The mixture was stirred for 1 hr., yielding a yellow solution with a fine yellow precipitate. Na_2mnt (0.137 g, 0.734 mmol) was then added neat and the mixture was stirred for 3 hrs, yielding a red-orange solution with a fine orange precipitate. The solution was then filtered, giving a red powder that was washed with 10 X 1 mL EtOH to give a dark red-orange $\text{Zn}(\text{mnt})(\text{Me}_2\text{Dt}^0)$ (0.2040 g, 0.537 mmol, 73%).

Characterization—Anal. Calcd. (experimental) for $\text{ZnC}_{10}\text{H}_{10}\text{N}_4\text{S}_4$: C, 31.62 (31.47); H 2.65 (2.65); N 14.75 (14.69), ^1H NMR (^1H , δ , ppm) in Acetonitrile: 3.94 (s, 6H, CH_3), 3.66 (s, 4H, CH_2). IR (cm^{-1}): 857.8 (m, C-S), 1366 (s, C=S), 1533 (s, C-N), 2197 (s, $\text{C}\equiv\text{N}$).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Synopsis

Crystallographically characterized bis-dithiolene Zn complexes with ligands of differing oxidation states exhibit low energy ligand to ligand (LLCT) charge transfer band.

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Figure 1.
Schematic representation of the Zn complexes reported here.

Figure 2. Electronic spectra of **1**, **2**, **3**, and **4** in acetonitrile; in the inset low energy ligand-to-ligand charge transfer bands are shown.

Figure 3.
Molecular structures of **1**, **2**, **3**, and **4** shown in 30% probability thermal ellipsoids with hydrogens omitted for clarity.

Figure 4. Solid state IR spectrum of **4** compared with DFT calculated vibrational frequencies. Dashed lines show precise diagnostic dithione ligand $\nu(\text{C}=\text{S})$ and $\nu(\text{C}-\text{N})$ peak predictions by DFT.

Figure 5.
A pictorial representation of frontier molecular orbitals and energies of **3**.

Figure 6.
Diagram of τ_4 and τ_8 angles, with α and β being two largest bond angles about the metal center.

Scheme 1.

Redox chemistry of a bis-dithiolene complex about a d_{10} metal center. Ligands in blue represent the fully oxidized dithione state while ligands in red represent the fully reduced dithiolate ligand state.

Table 1

General crystallographic information

	1	2	3	4
Chemical formula	C ₁₀ H ₁₈ Cl ₂ N ₂ S ₂ Zn	C ₆ H ₁₀ Cl ₂ N ₂ S ₂ Zn	C ₁₆ H ₂₁ N ₅ S ₄ Zn	C ₁₀ H ₁₀ N ₄ S ₄ Zn
M_r	366.65	310.55	476.99	379.83
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Temperature (K)	296	296	296	296
a (Å)	7.6235 (1)	9.6910 (4)	9.1445 (10)	10.2703 (1)
b (Å)	15.6390 (2)	9.4868 (4)	16.3139 (17)	12.8268(1)
c (Å)	13.3764 (2)	12.5107 (5)	15.3829 (16)	11.5909 (1)
β (°)	95.232 (1)	90.866 (3)	99.593 (6)	94.719 (1)
V (Å ³)	1588.14 (4)	1150.06 (8)	2262.8 (4)	1521.97 (2)
Z	4	4	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	2.13	2.92	1.46	2.15
Crystal size (mm)	0.23 × 0.20 × 0.07	0.17 × 0.09 × 0.01	0.56 × 0.07 × 0.05	0.39 × 0.35 × 0.25
No. of reflections: measured	9432	1474	30290	27787
independent	4846	1339	5099	5601
observed [$I > 2\sigma(I)$]	3858	1078	2758	4600
$R[F^2 > 2\sigma(F^2)]$	0.036	0.044	0.06	0.032
$wR(F^2)$	0.142	0.162	0.149	0.118
S	1.08	1.21	1.12	1.1
No. of reflections	4846	1339	5099	5601
No. of parameters	158	120	240	174
$\rho_{\max}$, $\rho_{\min}$ (e Å ⁻³)	1.23, -0.76	0.45, -0.38	1.08, -0.82	0.76, -0.57

Table 2

Select bond lengths (Å), angles and torsions (°).

	1	2	3	4
Zn-S (Dt ⁰)	2.3527(6), 2.3571(6)	2.364(2), 2.372(2)	2.326(2), 2.358(2)	2.3417(5), 2.3440(4)
Zn-Cl	2.2239(6), 2.2279(8)	2.213(2), 2.220(3)		
Zn-S (mnt)			2.285(2), 2.287(2)	2.2857(6), 2.2906(5)
C=S (Dt ⁰)	1.683(2), 1.686(2)	1.677(8), 1.682(9)	1.668(5), 1.681(1)	1.682(1), 1.683(1)
(N-C)-S	1.315(2), 1.316(2)	1.32(1), 1.32(1)	1.293(7), 1.315(6)	1.309(2), 1.310(2)
C-C (Dt ⁰)	1.525(3)	1.51(1)	1.536(7)	1.514(2)
C-S (mnt)			1.740(6), 1.731(5)	1.735(2), 1.738(2)
C=C (mnt)			1.354(7)	1.363(2)
Cl-Zn-Cl	110.50(3)	118.20(9)		
S-Zn-S (Dt ⁰)	91.07(2)	89.23(8)	89.29(5)	90.40(2)
S-Zn-S (mnt ²⁻)			95.96(5)	96.83(2)
S1-Zn-Cl1(S3)	116.54(2)	110.56(9)	111.81(5)	116.94(2)
S1-Zn-Cl2(S4)	109.71(3)	109.86(9)	125.12(6)	116.15(2)
S2-Zn-Cl1(S3)	111.94(2)	108.72(8)	122.03(5)	119.79(2)
S2-Zn-Cl2(S4)	116.03(3)	116.53(9)	115.17(6)	118.58(2)
S-C-C-S (Dt ⁰)	31.1(2)	-19(1)	19.9(5)	-24.6(2)
S-C-C-S (mnt ²⁻)			-0.8(7)	-0.1(2)

Table 3

Molecular orbital energies (eV) and percent compositions for frontier orbitals of **3** and **4**. The orbital contributions of the dithiolate ligand consider atoms (using the numbering scheme in Figure 3) S1, C1, C2, and S2. Orbital contributions of the dithione ligand consider atoms S3, C5, C6, S4, N3, and N4.

Orbital	Energy	Dithiolate	Dithione	Zinc
3				
107	-7.83	2	78	2
108	-7.69	38	25	12
109	-7.57	11	37	1
110	-6.56	76	14	1
111	-6.43	40	3	2
112	-5.08	42	19	1
113	-3.92	19	57	0
114	-1.85	2	27	1
115	-1.49	1	24	1
116	-1.11	62	17	1
117	-0.86	1	2	0
118	-0.83	20	39	3
4				
91	-8.06	8	84	1
92	-7.82	42	30	14
93	-7.69	19	51	2
94	-6.67	85	7	1
95	-6.55	43	1	2
96	-5.18	47	41	1
97	-4.17	37	35	1
98	-1.78	1	90	1
99	-1.54	2	82	1
100	-1.20	69	13	2
101	-0.94	3	67	0
102	-0.82	43	16	5

Table 4Calculated τ_4 and τ_8 values.

Compound	Chemical Formula	τ_4	τ_8
1	ZnCl ₂ (^a Pr ₂ Dt ⁰)	0.90	0.90
2	ZnCl ₂ (Me ₂ Dt ⁰)	0.89	0.88
3	Zn(mnt)(^a Pr ₂ Dt ⁰)	0.80	0.78
4	Zn(mnt)(Me ₂ Dt ⁰)	0.86	0.87
WOPWUV	[NEt ₃ Ph] ₂ [Zn(dmit) ₂]	0.78	0.78
CAYNUM	[C ₆ H ₈ N] ₂ [Zn(dmit) ₂]	0.86	0.81
DUHRON	[PPh ₄] ₂ [Zn(mnt) ₂]	0.83	0.77
DULFIZ	[AsPh ₄] ₂ [Zn(mnt) ₂]	0.82	0.77
FISMOJ	ZnCl ₂ (H ₂ dmdto)	0.90	0.90
JAFXET	[NEt ₄][Zn(dmid) ₂]	0.81	0.81
QUQGEO	Zn(mnt)(Py) ₂	0.81	0.74
RAXDAV	Zn(mnt)(4-Me-Py) ₂	0.88	0.88

 τ_4 and τ_8 values were calculated from structures of available Zn dithiolene ligand-containing complexes in the CSD.^a dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate.^b H₂dmdto = *N,N'*-dimethyl-dithio-oxamide.^c dmid = 2-oxo-1,3-dithiole-4,5-dithiolate.^d Py = pyridine.^e 4-Me-Py = 4-methylpyridine.