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Benzenthiolate bridged binuclear group 12 metal complexes with TTF fused dithiolate ligand, a new synthetic approach using cluster-cracking reaction†

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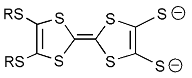
Novel binuclear dithiolate complexes $(Me_4N)_2[M_2(SPh)_2(S_2TTF(SMe)_2)_2]$ (M = Cd and Zn) have been synthesized by a new cluster-cracking method.

Charge-transfer salts based on TTF (tetrathiofulvalene or 2-(1,3-dithol-2-ylidnene)-1,3-dithiole) and dmit (4,5-dimercapto-1,3-dithiol-2-thione) systems have been studied extensively for their unusual electrical, magnetic and optical properties.[1] Recently, two areas that have been explored by inorganic chemists in this research effort are the synthesis and characterization of novel polynuclear coordination compounds and sulfur-rich ligands with extended conjugated systems. Up to now, a number of bimetallic complexes with formula $[C]_x\{tto[M(dmit)]_2\}$ [C = Bu_4N, Et_4N, Me_4N; tto = tetrathiooxalate, $C_2S_4{}^{2-}$; M = Cu(II), Ni(II)] have been isolated.[2] Also, in the syntheses of metal dithiolate complexes, a new type of ligand $[S_2TTF(SR)_2]^{2-}$, in which TTF and dmit are fused, has received much attention.[3] The extended conjugation and rich electrochemical behavior of this ligand implies good potential in applications to material chemistry.



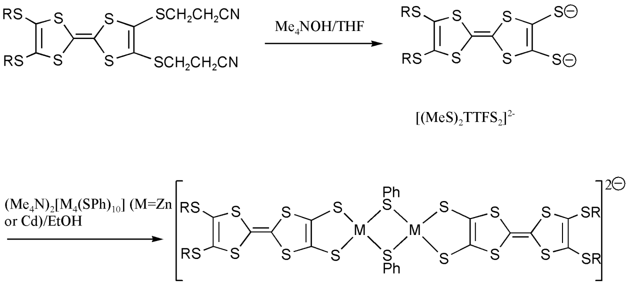
A number of research groups have prepared a series of mononuclear complexes with ligands $(RS)_2TTFS_2{}^{2-}$; besides the symmetric complexes, 'unsymmetric' complexes with formula $[M(S_2TTF(SR)_2)(diimin)]$ and $[M(S_2TTF(SR)_2)(Cp)]$ have also been explored.[4,5] To the best of our knowledge, polynuclear systems with this type of ligand have not been reported elsewhere. The tetranuclear cluster $[NMe_4]_2[Cu_4((MeS)_2TTFS_2)_3]$, which we first synthesized, is the only example.[6] McCullough's group has characterized some bimetallic coordination complexes with a tetrathiolate ligand.[7] In those reported metal complexes, the bridge is tetrathiolae $TTFS_4{}^{4-}$, an analog of $(RS)_2TTFS_2{}^{2-}$. The synthesis of binuclear TTF complexes, having an $M(X)_2M$ core (X = OR, SR *etc.*) is yet to be reported. Herein we report the synthesis and characterization of two novel benzenthiolate bridged binuclear group 12 metal complexes with a dithiolate ligand containing a TTF moiety.

Thiophenolate coordinated or bridged complexes are very common for transition metals, and numerous metal dithiolate complexes have been studied, though only a few thiophenolate/dmit mixed complexes have been reported.[1] Wu and Sheng reported the synthesis and structures of some mixed ligand dmit complexes with bridged alkyl dithiole, but their attempt to prepare heteroleptic complexes using thiophenolate failed.[8] Previously we have synthesized two unsymmetrical metal complexes $(Me_4N)_2[M(dmit)(SPh)_2]$ (M = Cd or Zn) by a new synthetic method: cluster-cracking reaction.[9] The complexes reported here were also prepared by this method (Scheme 1).

The precursor compounds of $(Me_4N)_2[M_4(SPh)_{10}]$ (M = Zn or Cd) were prepared by the method described in the literature.[10] 4,5-Bis(cyanoethylthio)-1,3-dithiol-2-[(4,5-dimethylthio)-1,3-dithiol-2-ylidene], $[(MeS)_2TTF(SCH_2CH_2CN)_2]$, was synthesized from the zinc complex of dmit according to the reported methods.[11] After deprotection of $[(MeS)_2TTF(SCH_2CH_2CN)_2]$ in THF using Me_4NOH, the resulting salt $(Me_4N)_2[S_2TTF(SMe)_2)]$ was added to $(Me_4N)_2[Cd_4(SPh)_{10}]$. The mixture was stirred for 1 h at room temperature forming an orange precipitate $(Me_4N)_2[M_2(SPh)_2(S_2TTF(SMe)_2)_2]$ (M = Cd **1** or Zn **2**).[12] The complexes were sealed in a glass tube under argon atmosphere to avoid oxidation. Although the growth of single crystals was not successful despite great effort, **1** and **2** were well characterized.

By use of the cluster-cracking method, both monomer (dmit ligand)[9] and binuclear complexes ($[S_2TTF(SMe)_2]^{2-}$ ligand, this work) can be prepared with high purity. However, a question arises as to why different structures are produced by the reaction of the clusters $(Me_4N)_2[M_4(SPh)_{10}]$ with the two similar dithiolene ligands under strictly identical reaction conditions (solvent, temperature, reagent quantities). To answer this question, a key point may relate to differences of electron density on the mercapto-sulfur atoms of the ligands. Since the coordination sphere of these complexes is a tetrahedron, the conjugating effect of the ligand planes on the metal ions is limited. Results calculated using the PM3 method revealed a difference in the charge on the mercapto sulfurs of the two ligands: −0.5927 for $dmit^{2-}$ and −0.5970 for $[(MeS)_2TTFS_2]^{2-}$, respectively. However, the structure (monomer or dimer) of the products, which were obtained by the same synthetic procedure, may also be influenced by the bulk of the ligands.

Over the last two decades, a considerable amount of papers has been published for the synthesis of clusters by the spontaneous self-assembly (SSA) of appropriate active segments and SSA has been proven successful in the synthesis of Fe/S or Fe/Mo/S clusters.[13] The simplest examples obtained from this method are clusters containing Fe_2S_2 and Fe_4S_4 cores. For example, two $[Fe_2S_2(NO)_4]^{2-}$ molecules are converted to $[Fe_4S_4(NO)_7]^-$ in acidic solution. These strategies are im-



Scheme 1 Synthetic reactions for the dinuclear complexes.

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† Electronic supplementary information (ESI) available: synthesis and characterization of the complexes. Fig. S1: ^1H NMR spectrum of **2**. Fig. S2: ES-MS of **1**. Fig. S3: PM3 calculated charges. See http://www.rsc.org/suppdata/cc/b2/b202698h/

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portant for the synthetic chemistry of clusters and are extensively used by inorganic chemists. In a reverse of SSA, we suggest a cluster-cracking strategy in which novel small dithiolate complexes can be synthesized from suitable bulky clusters by attack of dithiolate ligands[9] (see Graphical Abstract). Bulky clusters, such as $(Me_4N)_2[M_4(SPh)_{10}]$ (M = Zn or Cd), can some times be obtained conveniently. The structures of the final products are related to the nature of the attacking ligands and the leaving ligands.

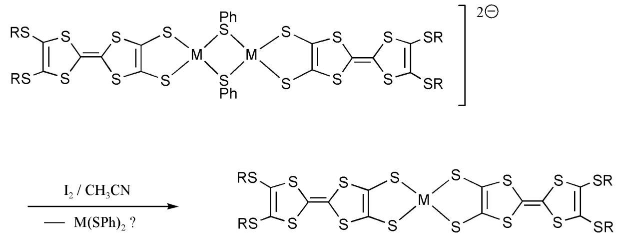
^{1}H NMR spectra of the complexes were measured in acetone-d$_6$. Three characteristic bands at 7.30 (t, 2H), 7.38 (t, 4H) and 7.55 (d, 4H) clearly indicate the presence of benzenthiolate in complexes **1** and **2**. In mono-complexes $(Me_4N)_2$[M(dmit)$(SPh)_2$] (M = Cd and Zn),[9] the chemical shifts of the bands for benzenthiolate are at 6.66 (t, 2H), 6.82 (t, 4H) and 7.51 (d, 4H), respectively. Since the ligand $[(MeS)_2TTFS_2]^{2-}$ carries more negative charge on the mercapto sulfur atoms than dmit^{2-} (discussed above), the significant downfield shifts of the signals relative to that of the mono-complexes provide evidence that the thiophenolate groups are bridged to the metals. This can be rationalized in that the electron density in bridged thiophenolate is shared by two metal centers. The suggested formulations are also in good agreement with the microanalyses.

Electrospray mass spectra of complex **1** in methanol–acetone were measured. The most strong peak is observed at *m*/*z* 581 is due to the $[Cd_2(SPh)_2(S_2TTF(SMe)_2)_2]^{2-}$ anion. The sulfur-rich complex is thermally unstable and as a result, some decomposition occurs at the measuring temperature (> 100 °C). Observed peaks at *m*/*z* 415 and 903 are due to the reassembled stable anions $[Cd(S_2TTF(SMe)_2)_2]^{2-}$ and $(Me_4N)[Cd(S_2TTF(SMe)_2)_2]^-$, respectively.

The IR peak of the C=C stretch of the TTF skeleton shifts to 1478 cm^{-1} in the Cd(II) complex **1** and Zn(II) complex **2** (relative to a value of 1487 cm^{-1} for the dithiolate salt $[Me_4N]_2[(S_2TTF(SMe)_2)_2]$), this is in accordance with the result for the copper(I) complex.[6] Three characteristic C–H stretches of the thiophenolate appear at 1574, 745 and 691 cm^{-1}. The electronic absorption spectra of complexes **1** and **2** in acetone were measured and are similar to each other. Strong ligand centered bands are located at 355, 380 and 490 nm. Intramolecular ligand-to-metal charge transfer (CT) transitions are very weak in these complexes due to the tetrahedron coordination of the metals.

Cyclic voltammetry (CV) showed three irreversible oxidations for **1** located at −0.17, 0.78 and 0.89 V *vs.* SCE. The first peak (−0.17 V) is expected to be due to the oxidation of the dithiolate coordinated center, and the others are considered to be due to oxidation of the TTF skeleton. Owing to its low first oxidation potential, this complex is easily oxidized even in the solid state under ambient conditions, with a change of color from orange to brown.

When acetonitrile solutions of **1** or **2** were oxidized by iodine, black precipitates which were insoluble in ordinary solvents formed immediately. Since the IR spectra clearly showed that C–H stretches of the thiophenolate disappeared in these oxidized compounds, they are unlikely to be the simple oxidized products of the complexes. The C=C frequencies of the TTF skeleton shift to 1451 and 1424 cm^{-1} upon oxidation. Together with the elemental analysis data, the products should be the neutral mononuclear complexes $[Cd(S_2TTF(SMe)_2)_2]$ (**3**) and $[Zn(S_2TTF(SMe)_2)_2]$ (**4**) (Scheme 2),[14] their insolubility, however, prevents further characterization. In fact, the dianionic version of **4** has been reported as precursor for synthesis.[4c,15] Electrical conductivities of these oxidized products have been measured by a two-probe method for compacted pellets at room temperature and values of 7.6×10^{-4} S cm^{-1} for **3** and 9.6×10^{-5} S cm^{-1} for **4** are obtained.



Scheme 2 Oxidation reaction of the dinuclear complexes.

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12 *Characterization*: complex **1**: yield 56%. Anal. for $C_{36}H_{46}N_2S_{18}Cd_2$: C, 33.08; H, 3.52; N, 2.14. Found: C, 33.47; H, 3.91; N, 2.61%. ^{1}H NMR (acetone-d$_6$): δ 2.40 (s, 12H), 3.42 (s, 24H), 7.31 (t, 2H), 7.38 (t, 4H), 7.55 (d, 4H). Complex **2**: yield 54%. Anal. for $C_{36}H_{46}N_2S_{18}Zn_2$: C, 35.64; H, 3.80; N, 2.31. Found: C, 35.74; H, 4.19; N, 2.54%. ^{1}H NMR (acetone-d$_6$): δ 2.40 (s, 12H), 3.42 (s, 24H), 7.30 (t, 2H), 7.38 (t, 4H), 7.53 (d, 4H).

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14 *Characterization*: complex **3**: yield 81%. Anal. for $C_{16}H_{12}S_{16}Cd$: C, 23.19; H, 1.45. Found: C, 22.82; H, 1.46%. Complex **4**: yield 78%. Anal. for $C_{16}H_{12}S_{16}Zn$: C, 24.58; H, 1.54. Found: C, 24.68; H, 1.77%.

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