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Synthesis, characterization, and crystal structures of molybdenum complexes of unsymmetrical electron-poor dithiolene ligands

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ABSTRACT

$Mo(S_2C_2(CF_3)_2)_3$, **1a**, has proven a useful p-dopant in organic electronics. To develop more soluble p-dopants, MoS_9^{2-} was treated with alkynes CF_3CCCO_2Me and $CF_3CCCOCF_3$ to give the dianions of the corresponding tris(dithiolene) complexes, $\mathbf{1b^{2-}}$ and $\mathbf{1c^{2-}}$, respectively, which were then oxidized to neutral molybdenum tris[1-(methoxycarbonyl)-2-(trifluoromethyl)-ethane-1,2-dithiolene], **1b**, and molybdenum tris[1-(trifluoroethanoyl)-2-(trifluoromethyl)ethane-1,2-dithiolene], **1c**, using $NO^+PF_6^-$. The crystal structures of $(NEt_4^+)_2\mathbf{1b^{2-}}$, $(NEt_4^+)_2\mathbf{1c^{2-}}$, and neutral **1c** have been determined. In all three cases, the metal coordination is approximately trigonal prismatic and the major isomer is *cis* (approximately C_{3v}). The structure of $\mathbf{1b^{2-}}$ is distorted by a twist towards pseudo-octahedral coordination similar to that seen in structures of $\mathbf{1a^{2-}}$ and $Mo(S_2C_2(CO_2Me)_2)_3^{2-}$, $\mathbf{1d^{2-}}$, salts, and that of **1c** exhibits marked folds between the planes formed by the ligand atoms and those formed by the Mo and coordinated S atoms, similar to those seen in the structure of **1a**. On the other hand, the metal dithiolene core of $\mathbf{1c^{2-}}$ is essentially undistorted from C_{3v} symmetry. The oxidant strength of the neutral molecules increases in the order **1d** < **1b** < **1a** < **1c**, with the potentials ranging from −0.02 to +0.39 V versus the ferrocenium/ferrocene couple.

1. Introduction

Molybdenum tris(dithiolene) complexes, $Mo(dt)_3$, along with other metal tris(dithiolene)s, have a variety of interesting characteristics: the metal coordination geometries are, unusually, (approximately) trigonal prismatic; the electronic structure is challenging to describe in a simple fashion, in part due to the "non-innocence" of the dt ligands (in Green's classification scheme of covalent compounds [1] dt can be regarded as either an X_2 or L_2 ligand and so there is ambiguity in assigning the valence number for the metal in neutral $M(dt)_3$ as 6, 0, or in between, and the electron number as 12, 18, or in between); and often multiple readily interconvertible redox states are isolable [2–12]. Moreover, Mo $(dt)_3$ and other molybdenum-dithiolene derivatives have been extensively used as models [13–21] for non-nitrogenase molybdenum-containing enzymes, a universal feature of which is a cofactor containing a Mo(dt) moiety [22]. Molybdenum tris(1,2-bis(trifluoromethyl)ethane-1,2-dithiolene), $Mo(tfd)_3$, **1a** (Fig. 1) also catalyzes various reactions of quadricyclane and norbornadiene [23]. **1a** and related compounds containing both the tfd and other dt ligands can also reversibly bind alkenes and may be useful models for heterogeneous reactions such as the deprotection of alkenes on Raney Ni and hydrodesulfurization reactions [24]. The magnetic properties and conductivity of salts formed by electron transfer between various donors and neutral $Mo(dt)_3$ acceptors have also been studied [25–28], while simple neutral $Mo(dt)_3$ complexes have recently been found to exhibit moderate two-photon absorption in the telecommunications region of the near infrared (NIR) [29].

Molecular redox doping of organic semiconductors is useful in a variety of different device types as a means of manipulating conductivity and charge injection or collection [30]. An ideal p-dopant should be strongly oxidizing, i.e. possess a high electron affinity (EA), and cleanly accept one electron from organic semiconductor materials to form an anion that is stable with respect to chemical reactions and to diffusion within the doped film, and that does

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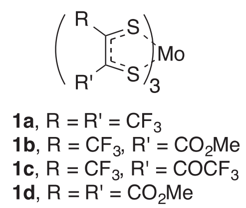
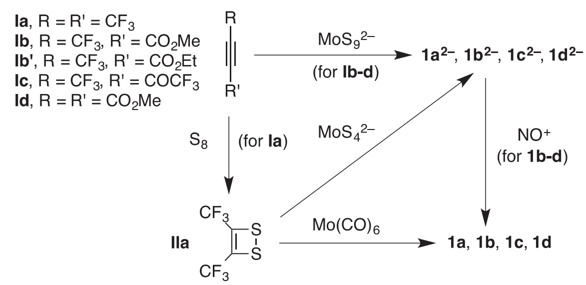


Fig. 1. Structures of $Mo(dt)_3$ complexes discussed in this work.



Scheme 1. Synthesis of some $Mo(dt)_3$ and $Mo(dt)_3^{2-}$ complexes reported in the literature or discussed in the present work.

not represent a deep electrostatic trap for carriers on adjacent semiconductor molecules. At the same time, the ideal dopant itself should be stable to ambient conditions and should be compatible with both vacuum and solution processing of doped films. One of the most widely used p-dopants is the planar molecule 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane [30], F_4-TCNQ ($E_{1/2}^{0/-}$ = +0.15 V versus $FeCp_2^{+/0}$ in CH_2Cl_2 [31], EA(s) = 5.2 eV [32]), which, however, is poorly soluble in many solvents [33], is rather volatile with a poor sticking coefficient [34,35], is rather prone to diffusion within doped films [32,34–37], and, due to its planarity, can form charge-transfer complexes with a number of organic semiconductors rather than undergoing an electron-transfer reaction [38,39].[1] Inspired in part by the work of Malcolm Green and co-workers in using **1a** (Fig. 1) as an acceptor in electron-transfer reactions to form molecular salts [25–27], we considered that this molecule, which was the most strongly oxidizing $Mo(dt)_3$ derivative to have been isolated in its neutral state, might be a useful p-dopant. Subsequently, work carried out in collaboration with Kahn and Kippelen [31,40–42], as well as independent work by others [43,44], has confirmed that **1a** is indeed an effective p-dopant for hole-transporting materials including triarylamine-based compounds and pentacene. Compared to F_4-TCNQ, **1a** has a slightly more anodic molecular reduction potential and higher solid-state EA (*vide infra*), has a higher molecular weight that allows for more controllable sublimation, forms an anion subsequent to doping that is less prone to diffusion within doped films [31,40], and, due to its 3D shape, might be expected to exhibit a reduced tendency towards charge-transfer complex formation (although DFT calculations suggest that such complex formation may still occur with certain donors [45]). It has also been reported that **1a** leads to higher efficiencies of generation of "free" carriers in semiconductors than the vacuum-processible inorganic dopants ReO_3 and MoO_3, even though the oxides are stronger oxidants; this has been attributed to a more homogenous dispersion of the molecular dopants in the organic matrix than for the oxide dopants, which phase segregate to form crystalline nanoclusters [44]. However, although both evaporated and solution-processed semiconductor films are used in organic electronics, to date the use of **1a** as a dopant has been largely restricted to evaporated films. Its solubility in common organic solvents is not particularly high, although perhaps sufficient for spin-coating using typical dopant concentrations; however, in some cases organic semiconductors heavily doped with **1a** are found to precipitate from solution, precluding processing of these materials. Accordingly, we were interested in developing derivatives of **1a** with substituents that increase both the solubility of the neutral species and of salts formed with oxidized semiconductor molecules and polymers, and that allow the oxidant properties of **1a** to be largely retained. We have recently reported on doping of organic semiconductors and of graphene using two such compounds, **1b** and **1c** [46–49]; here we report more fully on their synthesis, spectroscopy, electrochemistry, and crystal structures.

2. Experimental

2.1. General considerations

Experimental details for the syntheses of $(NEt_4^+)_2$**1b**$^{2-}$ [47], **1b** [47], $(NEt_4^+)_2$**1c**$^{2-}$ [46], and **1c** [46] according to Scheme 1 have been published elsewhere. Compound **1a**, used for comparison, was synthesized according to the literature [50]. UV–Vis-NIR spectra were recorded in 1 cm cuvettes using a CARY 5000 spectrometer. Electrochemical measurements were carried out in dry deoxygenated dichloromethane containing 0.1 M $NBu_4^+PF_6^-$ using a BAS potentiostat, a glassy carbon working electrode, a platinum wire auxillary electrode, and pseudo-reference electrode consisting of a silver wire coated with AgCl by anodization in aqueous K^+Cl^- solution. $CoCp_2^+PF_6^-$ was used as an internal standard to reference potentials to the $FeCp_2^{+/0}$ couple ($E[CoCp_2^{+/0}] = -1.32$ V versus $FeCp_2^{+/0}$) [51].[2]

2.2. Synthesis of **1d**

Dimethyl but-2-ynedioate, **Id** (0.77 g, 5.42 mmol) was added by syringe to a suspension of $(NEt_4^+)_2MoS_9^{2-}$ (1.00 g, 1.55 mmol) [52] in deoxygenated MeCN (10 mL) under nitrogen. The reaction mixture was stirred at room temperature for 1 h, and at 50 °C for 22 h, during which time its color turned from red-brown to dark blue. After cooling, the reaction solution was filtered through Celite and the volatiles were removed under reduced pressure. The dark blue semi-solid was dissolved in CH_2Cl_2 and then MeOH was added. The CH_2Cl_2 was removed under reduced pressure and the MeOH solution was cooled at −80 °C overnight, affording a dark blue solid, which was collected by filtration and washed with MeOH. This process of dissolution, MeOH addition, evaporation, cooling, and filtering was repeated five times to give a dark blue solid (1.10 g). The reaction was also carried out on a 10× greater scale to give 12.0 g of the crude salt. The combined crude product (13.0 g) was purified by Soxhlet extraction into dichloromethane to give purer $(NEt_4^+)_2$**1d**$^{2-}$ (8.5 g), which, however, still contained impurities. ^1H NMR (400 MHz, acetonitrile-d_3): δ 3.70 (s, OCH_3, 18H), 2.95 (q, J = 7.6 Hz, 16H, NCH_2), 1.08 (t of 1:1:1 t, J_{HH} = 7.6 Hz, J_{NH} = 2.0 Hz, 24H, Et CH_3). Excess $NO^+PF_6^-$ (0.80 g, 4.6 mmol) was added to a solution of the impure salt (1.0 g) in CH_2Cl_2 (30 mL) and stirred at room temperature under nitrogen for 2 h; the course of the reaction was monitored by UV–Vis. absorption spectroscopy. The color of the solution turned from dark green-blue to blue and brown gas was evolved. The reaction mixture was filtered to remove insoluble impurities, the CH_2Cl_2 was removed under reduced pressure, and the resulting dark blue solid was extracted with benzene (150 mL). The benzene extracts were concentrated

[1] For some organic p-dopants that have been developed to address some of these drawbacks of F_4-TCNQ, see, for example, Refs. [34,35,37].

[2] $FeCp_2$ itself was not used as a reference since its oxidation overlaps with the reduction of some of the $Mo(dt)_3$ compounds examined here.