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1, 1'-DITHIOLENES: THE GOOD, THE NOT BAD, AND THE UGLY

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A series of 1, 1'-dithiolate ligands were used in the attempted preparation of metal complexes. These bidentate sulphur ligands were subsequently used in aromatic nucleophilic substitution reactions giving rise to several novel organic donor molecules. The electrochemistry data of two of the donors and their subsequent use in the preparation of donor-acceptor compounds is presented. One donor-acceptor compound exhibited high room temperature conductivity (up to 900 S cm^{-1}) and remained metallic down to low temperature. One donor containing two tetrathiafulvalene units was studied by near infrared absorption spectroscopy. An intervalence transition in the monocation form of this donor was observed, indicating that it behaves as a class II mixed valence compound.

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1. Introduction

Over the past twenty years, many compounds which display metallic properties at room temperature and below have been synthesized, many of which are based on the organic donor molecule, tetrathiafulvalene (TTF) [1] as shown in Fig. 1.

Metal bis(1,2-dithiolene) complexes have a central core structurally analogous to the TTF molecule and have been extensively studied [2]. Most work has concentrated on the salts of $[\text{M}(\text{dmit})_2]^{x-}$ (Fig. 1), where $\text{M} = \text{Ni}, \text{Pd}$ or Pt , with

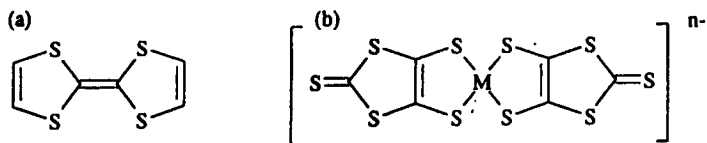


Fig. 1. (a) The donor molecule tetrathiafulvalene, TTF, and (b) the metal bis(1,2-dithiolene), $[M(dmit)_2]$. (H_2dmit = dimercaptoisotrithione or 4,5-dimercapto-1,3-dithiole-2-thione).

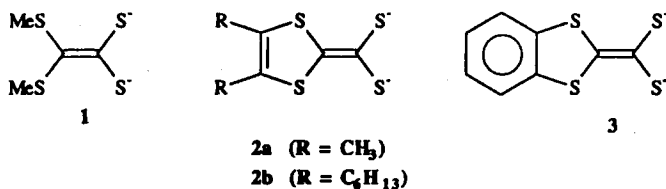


Fig. 2. 1,1'-dithiolate ligands used in the attempted preparation of metal bis(1,1'-dithiolate) complexes.

a variety of open shell organic cations, closed shell organic cations and with alkali metal cations [2]. Much less effort has been devoted to chemical modification of the ligand itself. Therefore, following the synthesis [3] of a new series of 1,1'-dithiolate ligands (Fig. 2), we attempted the formation of metal bis(1,1'-dithiolene) complexes derived from these ligands.

The results, and subsequent directions of research arising therefrom, are presented here.

2. Results and discussion

2.1. Attempted preparation of metal bis(1,1'-dithiolates)

The attempted synthesis of metal complexes derived from ligand 2a (Fig. 2) was carried out as shown in reaction scheme (Fig. 3) either by (a) direct use of the non-isolated dianion or (b) deblocking of the thiol ester.

Despite multiple attempts involving changing the solvent, the metal, the counter-cation and even the temperature of the reaction, in each case an insoluble amorphous powder was obtained. The negative ion fast atom bombardment (FAB) mass spectrum showed no peak of an m/z corresponding to that anticipated for the metal complex anion. Further experiments using the ligands 1 and 3 (Fig. 2) under various conditions gave similar results, i.e. insoluble amorphous powders that denied identification. Work is now continuing to overcome the problem of insolubility by the incorporation of long alkyl chains on the periphery of the dithiolate ligand, 2b (Fig. 2), which may allow the subsequent identification of these products.

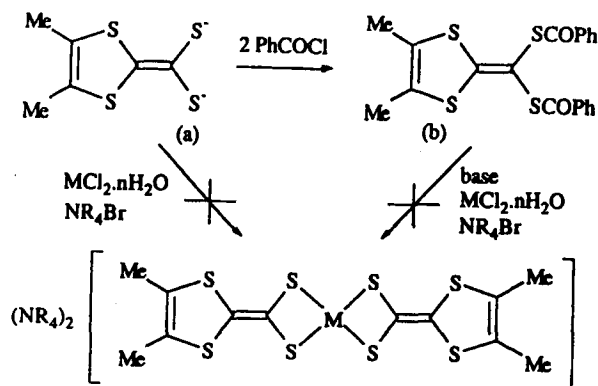


Fig. 3. The attempted syntheses of metal bis(1,2-dithiolato) complexes derived from 2a.

2.2. Synthesis of donors derived from the 1, 1'-dithiolate ligands

These bidentate sulphur anions have been shown [3, 4], however, to undergo aromatic nucleophilic substitution reactions giving rise to a range of donor molecules [3], two of which are presented in Fig. 4.

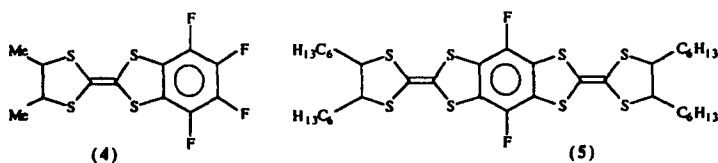


Fig. 4. Donors derived from the 1, 1'-dithiolato ligands 2a and 2b.

The electrochemical data for these donors are presented in Table. Donor 4 (Fig. 4) exhibits two completely reversible one-electron redox processes,

TABLE

Electrochemical data for the donors 4 and 5.

Donor	$E_{1/2}^1$	$E_{1/2}^2$	$E_{1/2}^3$	$E_{1/2}^4$
4 ^(a)	0.63	1.11		
5 ^(a)	0.52	0.69	1.18	1.78
TTF ^(b)	0.31	0.68		

Experimental conditions: (a) 10^{-3} M in donor, 10^{-1} M in supporting electrolyte (tetra-butylammonium hexafluorophosphate) at a 2 mm Pt electrode vs. SCE in dichloromethane; (b) 10^{-3} M in donor, 10^{-1} M in supporting electrolyte (tetra-butylammonium hexafluorophosphate) at a 2 mm Pt electrode vs. Ag/Ag⁺ in acetonitrile.

and donor 5 (Fig. 4) shows four one-electron reversible redox waves, consistent with the presence of two interacting TTF centres.

Although the first oxidation processes of these donors are displaced to higher potentials when compared to TTF, they were studied further in the formation of donor-acceptor complexes.

2.3. Conducting donor-acceptor complexes

When the donors were allowed to react with $(\text{NBu}_4)[\text{Ni}(\text{dmit})_2]$ or $(\text{NBu}_4)[\text{Pd}(\text{dmit})_2]$, either by electrocrystallization or diffusion methods [2], large black needles or platelets were obtained in each case. Preliminary four-probe conductivity measurements on the compound (4) $[\text{Ni}(\text{dmit})_2]_x$ show it to have a room temperature conductivity, σ_{RT} , of up to 900 S cm^{-1} and to display metallic behaviour down to 220 K (Fig. 5a).

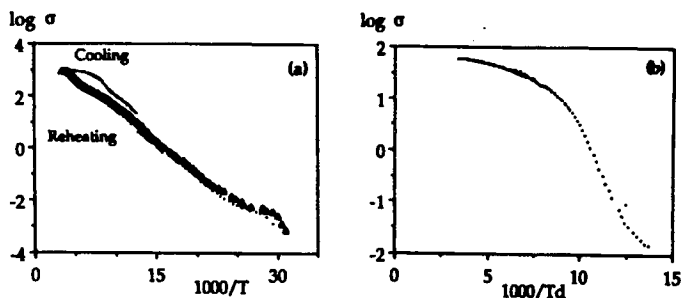


Fig. 5. Conductivity behaviour of (a) (4) $[\text{Ni}(\text{dmit})_2]_x$ and (b) (5) $[\text{Pd}(\text{dmit})_2]_x$.

At this temperature it undergoes a semiconductor transition, and remains semiconducting down to 70 K. When the cooled sample is reheated stepwise to room temperature, it is seen to exhibit a large hysteresis, regaining its metallic behaviour at 270 K, and eventually regaining its previous σ_{RT} . On the other hand, the complex (5) $[\text{Pd}(\text{dmit})_2]_x$ exhibits a σ_{RT} of 60 S cm^{-1} but is semiconducting over the entire temperature range studied (Fig. 5b).

2.4. A new organic mixed valence system

The electrochemistry results of donor 5 were comparable to those of similar bis-TTF systems [5], i.e. this compound undergoes four one-electron reversible oxidations, consistent with the sequential formation of the mono-, di-, and tetracationic species. These results are also consistent with two electronically interacting TTF units coupled via a π conjugated bridge. The formal similarity between the monocation of compound 5 containing non-equivalent "oxidation states" on both TTF units, and organometallic mixed valence complexes in which two metal centres joined by a bridging ligand can exist in two different oxidation states [6], was remarked. One important property of these mixed valence complexes is the intervalence transfer band (IT) [6, 7] corresponding to a light-induced charge transfer between the metal centres. A study of the solution absorption properties was

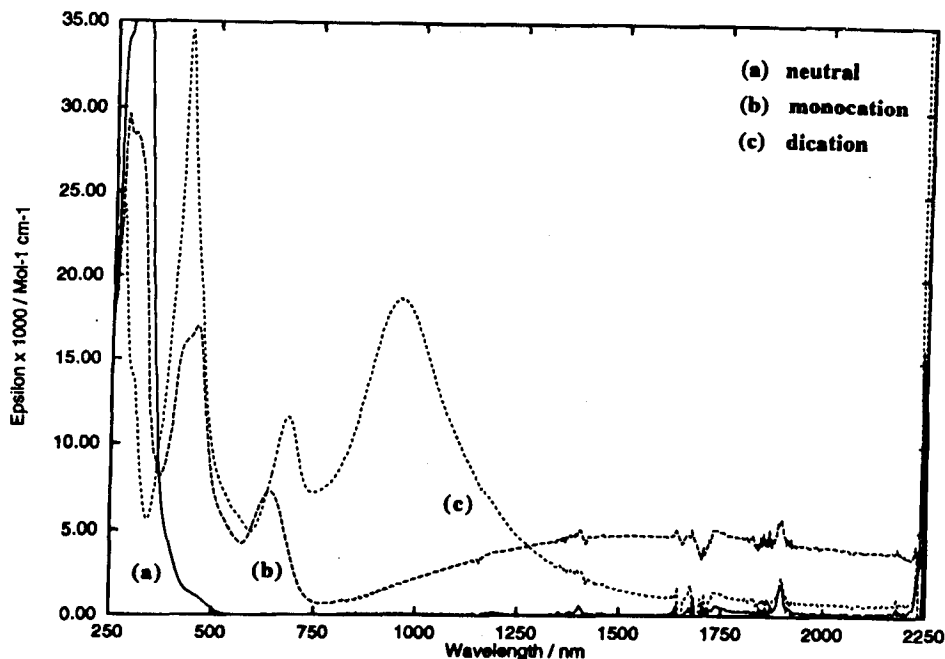


Fig. 6. NIR absorption spectrum of (5), (a) neutral, (b) monocation, and (c) dication in dichloromethane using 2 mm quartz cells.

therefore effected for the donor 5. The neutral unoxidized form revealed a weak absorption band in the visible region (Fig. 6), as is normal for TTF derivatives.

The monocationic "mixed valence" form was prepared by electrolysis and its UV-Vis-NIR spectrum measured, revealing the formation of an intense NIR band between 1000 and 2000 nm. Further oxidation to the diradical cation caused the disappearance of this band, consistent with the formation of an electronically symmetrical species. Calculations on the nature of the transition have shown this donor to be a class II material according to the Robin and Day classification [8], consistent with a partially delocalized system. Further experiments and ESR data for 5, as well as several other novel donors, will be given elsewhere [9].

3. Conclusion

The consequences of this result are far-reaching, in areas such as biology, solid state chemistry, inorganic reaction mechanisms and the emerging field of molecular electronics are highly dependent upon intra-molecular electron transfer. This new source of organic mixed valence materials is of particular interest as the synthetic versatility of organic donor molecules will permit a systematic investigation into the rate of decay of the electronic interaction between the two redox sites as a function of distance, something that is of considerable current interest [7].

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