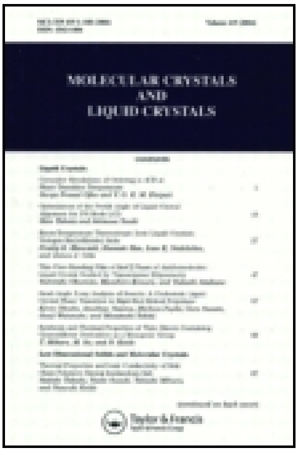

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New Molecular Conductors Based on Metal Complex Anions

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NEW MOLECULAR CONDUCTORS BASED ON METAL COMPLEX ANIONS

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Abstract The preparation and electrical conduction properties of $[TTF]_3[Au(dmit)_2]_2$, $[TMTSF]_3[Au(dmit)_2]_2$ and $[BEDT\text{-}TTF][Au(dmit)_2]$ are described. The electrical conduction properties of the products obtained by the electrocrystallisation of $[TEA]_2[Ni(dmid)_2]$ in the presence of a large excess of Group 1 cations are described and compared with the corresponding products obtained using $[TBA]_2[Ni(dmit)_2]$.

INTRODUCTION

Recently there has been increasing research activity in the search for new molecular metals and new molecular superconductors based on metal complex anions. There are now four low temperature molecular superconductors based on the $[M(dmit)_2]$ anions [1-3]. Three of these compounds contain the radical cation TTF whilst the fourth $[(CH_3)_4N][Ni(dmit)_2]_2$ contains the spectator ion $[(CH_3)_4N]^+$ as the counter ion and therefore the superconducting properties of this latter salt must involve only the metal complexed anion [3].

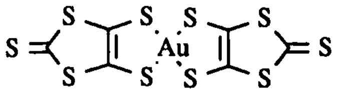
As part of a programme of research into the development of new molecular metals and molecular superconductors we have been studying the effect of

(a) modifying the ligand,

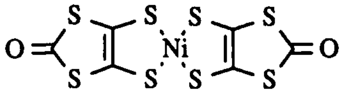
(b) changing the counter cation,and

(c) changing the central metal atom

on the properties of this type of molecular metal. In this paper we discuss some of the results of this strategy.



$[Au(dmit)_2]$



$[Ni(dmid)_2]$

RESULTS AND DISCUSSION

(a) New Conducting Charge-transfer Salts of $[Au(dmit)_2]^-$ with Open Shell Cations.

Electrocrystallisation of solutions of TTF, TMTSF or BEDT-TTF and $TBA[Au(dmit)_2]$ produced the new charge transfer salts $[TTF]_3[Au(dmit)_2]_2$, $[TMTSF]_3[Au(dmit)_2]_2$ or $[BEDT\text{-}TTF][Au(dmit)_2]$. Unfortunately, the size of the crystals was not sufficient for either the determination of their X-ray structure or for single crystal electrical conduction studies. The electrical conductivity of a compressed pellet of the TTF and TMTSF salts at room temperature gave conductivities of 1.2×10^{-1} and 6.5×10^{-2} S cm^{-1} respectively. $[BEDT\text{-}TFF][Au(dmit)_2]$ gave a significantly lower conductivity of 1.8×10^{-4} S cm^{-1}. All three compounds exhibited decreasing conductivity with decreasing temperature with activation energies of approximately 0.06, 0.03 and 0.23 eV for the TTF, TMTSF and BEDT-TTF salts respectively.

The 3:2 stoicheiometry of the TTF and TMTSF salts has not been seen before for $[M(dmit)_2]$ complexes. Previous TTF charge transfer salts of $[M(dmit)_2]$ have exhibited a 1:2 stoichieometry where M = Ni, Pd, or a 1:3 stoicheiometry where M = Pt.[4] In addition, the compound $TMTSF[Ni(dmit)_2]$ has been reported.[5] Work is currently in progress to grow better quality crystals of these salts to enable more detailed structural and solid state properties to be determined.

(b) Salts of $[Ni(dmid)_2]$ with Group I Cations.

One of the possible modifications to the dmit ligand is to convert the thiol group into a ketone (dmid).[6] The replacement of sulphur by oxygen on the periphery of the ligand will not be expected to have any significant steric effect. However, it may change the properties of the complexes compared with those involving the dmit ligand in two ways.

(i) There will be some change in intermolecular interactions due to the replacement of S...S by O...O interactions.

(ii) The presence of the more electronegative oxygen will also be expected to change the electron distribution in the HOMO and this will affect both the intramolecular bonding and intermolecular interactions involving the complex anion

Previous studies on $[Ni(dmid)_2]$ salts have included the preparation of the TTF salt and those of large spectator counter ions such as TBA and $AsPh_4$. We have recently shown that electrocrystallisation of $TBA_2[Ni(dmit)_2]$ in the presence of a larger excess of a group I counter cation produces compounds of stoicheiometry $M[Ni(dmit)_2]_2$. The sodium and potassium salts have been shown to be molecular metals at room temperature and, indeed, the sodium salt remains metallic down to 25 mK.[7,8]

Electrocrystallisation of solutions of $TEA_2[Ni(dmid)_2]$ in the presence of an excess of a group I cation produced micro-

crystalline products in the case of Li^+, Na^+, K^+, but no products were obtained in the presence of Rb^+ and Cs^+. A product was also obtained in the presence of Ba^{2+}.

The conductivities of these compounds have been examined in the form of compressed pellets. The lithium salt exhibited a room temperature conductivity of 0.006 S cm^{-1} and behaved as a semiconductor on lowering the temperature with an activation energy of 160 meV. The sodium compound exhibited a room temperature conductivity of 10 S cm^{-1} and again behaved as a semi-conductor on lowering the temperature with an activation energy of 105 meV. The K^+ salt exhibited a room temperature conductivity of 0.16 S cm^{-1} and it again behaved as a semi-conductor with an activation energy of 125 meV. The Ba^{2+} gave figures of 0.07 S cm^{-1} and 135 meV respectively.

A comparison of these results with those of the corresponding dmit complexes is difficult since only compressed pellet measurements are available or the dmid complexes whereas single crystal measurements have been reported for some of the corresponding dmit complexes.[7,8] It is noteworthy, however, that the sodium salt of $[Ni(dmid)_2]$ exibits a very high room temperature conductivity for a compressed pellet sample and it is the sodium salt in the $[Ni(dmit)_2]$ series of complexes which retains its metallic properties down to 25mK.

The experiments carried out so far would suggest that it is harder to grow single crystals of the dmid complexes than those of dmit. This may be a reflection of the differences in the structure of these two compounds and suggests that the presence of the keto group does not facilitate crystal growth.

EXPERIMENTAL

1. Preparation of Starting Materials

Dmit-thiol ester

The dmit ligand was produced according to the method of Steimecke *et al* via reduction of carbon disulphide with sodium metal.[9] The sodium salt was converted to the dithiol ester via benzoyl chloride and stored until needed.

Dmid-thiol ester

The dmid-thiol ester was produced from the dmit-thiol ester according to the method of Fanghanel *et al* via oxidation of the thione function with mercuric acetate and acetic acid in chloroform.[6] The ester was recrystallised from chloroform/methanol and stored until needed.

TBA [Au(dmit)$_2$]

To 812 mg (2 mmol) of dmit-thiol ester, suspended in 10 cm^3 dry degassed methanol under an argon atmosphere, was added an excess of sodium methoxide (0.2 g sodium) in 20 cm^3 dry degassed methanol and the mixture left sitrring for 20 min under argon. To the mixture was added dropwise sequentially, 3 cm^3 0.880 gcm^{-3} ammonia solution, 330 mg (1 mmol) tetrabutylammonium bromide in 10 cm^3 methanol and 340 mg (1 mmol) chloroauric acid in 10 cm^3 methanol. The mixture was left stirring for 30 min and then filtered and washed with methanol (5 cm^3) and anhydrous diethyl ether (20 cm^3). Recrystallisation from acetonitrile gave brown needle crystals. (Found: C, 30.99; H, 1.25; N, 4.29%. Calc. for $AuC_{22}H_{36}NS_{10}$:
C, 31.77; H, 4.33; N, 1.68%.)

TEA$_2$[Ni(dmid)$_2$]

To 780 mg (2 mmol) dmid-thiol ester in 10 cm^3 dry degassed methanol under an argon atmosphere, was added an excess of sodium methoxide in dry degassed methanol (0.2 g sodium reacted with 20 cm^3 methanol) and the mixture stirred under argon for 20 minutes.

To this mixture was added dropwise with stirring 420 mg (2 mmol) tetraethylammonium bromide dissolved in 10 cm^3 dry degassed methanol followed by 600 mg (1 mmol) tetraethylammonium nickel tetrabromide dissolved in 10 cm^3 dry degassed methanol. The mixture was stirred for 30 min and the product filtered off and washed with dry degassed methanol and then with anhydrous diethyl ether. The product was recrystallised from acetonitrile to give green crystals, M.pt. >350°C. (Found: C, 37.81; H, 4.15; N, 3.70%. Calc. for $NiC_{22}H_{48}N_2S_{10}$: C, 38.88; H, 5.89; N, 4.12%.)

Preparation of Group I Salts

To 0.1 g TEA$_2$[Ni(dmid)$_2$] in 50 cm^3 dry degassed acetonitrile was added 50 cm^3 dry degassed acetonitrile containing 25x molar excess of the appropriate group I salt as the hexafluorophosphate or perchlorate. The mixture was then filtered into a 100 cm^3 two-necked round-bottommed flask and two platinum electrodes fitted. The apparatus was connected to a constant current supply of 2 μA. After one day the anode was replaced and the experiment continued for 2 weeks. The microcrystalline powder which formed on the electrodes was collected, washed with anhydrous diethyl ether and dried in a vacuum oven.

$[TTF]_3[Au(dmit)_2]_2$

TTF (40 mg) and $[Bu_4N][Au(dmit)_2]$ (80 mg) were dissolved in dry degassed acetonitrile (60 cm^3) and transferred to a two-compartment H cell fitted with a porosity 3 frit. Electrocrystallisation was carried out at 20°C at a constant current of 2.00 μA. After 3 days scaly overgrown black plates were collected from the anode. Three more crops of crystals were collected over a two-week period (Found; C: 20.63, H: 0.65%. Calc. for $C_{30}H_{12}Au_2S_{34}$; C: 20.10, H: 0.67%).

$[TMTSF]_3[Au(dmit)_2]_2$

TMTSF (30 mg) was dissolved in the dark in dry degassed 1,1,2-trichloroethane (30 cm^3) and transferred to a 100 cm^3 three-necked round-bottomed flask. To this was added a solution of $[Bu_4N][Au(dmit)_2]$ (80 mg) in dry degassed acetonitrile (60 cm^3). The solution was allowed to stand for 3 hours during which time some precipitation of TMTSF occurred. Electrocrystallisation was carried out at a constant current of 1.00 μA. Extremely thin lustrous blue-black needles grew on the anode within 1 hour, these were harvested after 1 day. A second drop was grown at 0.50 μA but showed no improvement in crystal quality. (Found: C, 20.68; H, 1.49%. Calc. for $C_{42}H_{36}Au_2S_{20}Se_{12}$: C, 20.00; H, 1.44%.)

$[BEDT\text{-}TTF][Au(dmit)_2]$

BEDT-TTF (20 mg) was dissolved in dry degassed 1,1,2-trichloroethane (20 cm^3) and transferred to the anode chamber of a two compartment H cell fitted with a porosity 3 frit. $[Bu_4N][Au(dmit)_2]$ (40 mg) was dissolved in dry degassed acetonitrile (60 cm^3), this was split into 40 cm^3 and 20 cm^3 portions which were added to the cathode and anode chambers of the H cell respectively. The solution was allowed to stand for 3 hours during which time some BEDT-TTF precipitated in the anode chamber. Electrocrystallisation was carried out at 20°C at a constant current of 2.00 μA. Shiny black overgrown crystals formed on the anode and were collected after 2 days. A second crop was collected after a further 2 days. (Found: C, 19.54; H, 0.77%. Calc. for $C_{16}H_8AuS_{18}$: C, 19.72; H, 0.83%.)

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