Studies on the Salts of Planar Metal Dithiolate Anions with the Redox Active 3,7-Bis(dimethylamino)phenothiazin-5-ium Cation (Methylene Blue) †

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The preparation of two series of 3,7-bis(dimethylamino)phenothiazin-5-ium (methylene blue, mb) salts with $[M\{S_2C_2(CN)_2\}_2]^{2-}$ and $[M\{S_2C_2(CN)_2\}_2]^-$ (M = Ni, Pd, Pt, or Cu) is described. Compressed pellets of all these compounds exhibit conductivities of less than $10^{-5}\ \Omega^{-1}\ cm^{-1}$ at room temperature. Single crystals of $[mb][Pt\{S_2C_2(CN)_2\}_2]$ behave as semiconductors with an activation energy of 238 meV and a room-temperature conductivity of $10^{-5}\ \Omega^{-1}\ cm^{-1}$.

The discovery of a new type of one-dimensional metallic complex based on square-planar metal dithiolate anions has aroused renewed interest in the metal dithiolate salts.[1,2] The partially oxidised metal dithiolate complex $Li_{0.82}[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$ [$S_2C_2(CN)_2$ =(*Z*)-1,2-dicyanoethen-1,2-dithiolate, maleonitriledithiolate (mnt)] with its metallic properties contains a columnar stack of eclipsed metal dithiolate anions with equidistant Pt ··· Pt distances along the stack.[3] The small hydrated cations facilitate short inter-anion separation, and along with extensive neighbouring molecular orbital overlap and hydrogen bonding, give rise to the high metallic conductivity. Salts of bulky cations (*e.g.* $[NEt_4]^+$) only occur as simple 1 : 1 or 2 : 1 salts and possess much lower conductivities due to non-equivalent Pt ··· Pt distances.[4] The one-dimensional metal '$(perylene)_2[Pt(mnt)_2]$' contains planar organic cation stacks and conduction occurs through the cations rather than through the dithiolate anions.[5]

As an extension of this work, extensive studies have been made of the salts of planar dithiolates with the planar organic cation 3,7-bis(dimethylamino)phenothiazin-5-ium (commonly called methylene blue, mb). Methylene blue was chosen for its planarity, solubility, redox nature (having stable $[mb]^+$ and neutral mb^0 forms) and the relatively high conductivity observed for the chloride salt: *ca.* $10^{-6}\ \Omega^{-1}\ cm^{-1}$.[4] Thus the mb salts of metal dithiolate anions have the potential for conduction either through the planar anion or cation stacks, or more unusually through a combination of both donor and acceptor stacks. Rosseinsky and Malpas[4,6] have pioneered this field by showing that the $[mb]^+$ salts of $[Ni(mnt)_2]^{n-}$ (n = 1 or 2) have higher conductivities than the corresponding $[NEt_4]^+$ salts.

Experimental

Preparation of Simple Salts.—The $[mb]_2[M(mnt)_2]$ (M = Ni, Pd, Pt, or Cu) salts were prepared by the direct combination of 2 : 1 mol equiv. of [mb]Cl and $[NEt_4]_2[M(mnt)_2]$ in acetonitrile. This gave an immediate microcrystalline product and yielded a purer product than alternative reported methods.[7] The $[mb][M(mnt)_2]$ salts were prepared in a similar manner from a 1 : 1 mol equiv. of $[NEt_4][M(mnt)_2]$ and [mb]Cl in acetonitrile.[8] Chemical analyses of the salts are given in Table 1.

Table 1. Analysis of compounds

	Analysis * (%)		
Compound	C	H	N
$[mb]_2[Ni(mnt)_2]$	52.00	3.95	14.85
	(52.95)	(4.00)	(15.45)
$[mb]_2[Pd(mnt)_2]$	50.85	3.95	13.95
	(50.30)	(3.80)	(14.65)
$[mb]_2[Pt(mnt)_2]$	46.75	3.50	13.50
	(46.00)	(3.45)	(13.40)
$[mb]_2[Cu(mnt)_2]$	52.05	3.90	15.20
	(52.65)	(4.00)	(15.35)
$[mb][Ni(mnt)_2]$	46.35	2.85	15.70
	(46.25)	(2.90)	(15.75)
$[mb][Pd(mnt)_2]$	42.75	2.75	13.20
	(42.95)	(2.70)	(14.60)
$[mb][Pt(mnt)_2]$	38.10	2.55	13.05
	(37.95)	(2.40)	(12.90)
$[mb][Cu(mnt)_2]$	45.90	2.90	15.65
	(45.90)	(2.90)	(15.60)

* Calculated values are in parentheses.

Attempts were made to obtain single crystals of the 2 : 1 and 1 : 1 salts by recrystallisation of the products obtained above from the following solvent systems: CH_3Cl, $MeOH-H_2O$, Me_2CO, CH_2Cl_2, $CHCl_3$, MeOH, Me_2CO-Bu^tOH, dmso (dimethyl sulphoxide), dmso–EtOH, dmso–dmf (*NN*-dimethylformamide), and dmf. However, most of these recrystallisations resulted in a microcrystalline product. When dmf was used as the solvent the recrystallisation occasionally gave a few gold coloured crystals. The crystals varied in shape from needles to flakes but were too few and too fragile to allow separation from the bulk of the powdered product. Gold flakes were also obtained when recrystallising $[mb][Pd(mnt)_2]$ from dmso. However, it was not possible to separate the flakes into single crystals. The largest yield of crystals came from the recrystallisation of $[mb][Pt(mnt)_2]$ from dmf. The flat, black needle crystals were deposited when the hot dmf was allowed to cool.

Attempted Preparation of Non-stoicheiometric $[M(mnt)_2]$ (M = Pd or Pt) *Salts.*—Both chemical and electrochemical preparations of $[mb]_x[M(mnt)_2]$ (where x is non-stoicheiometric and <1) were attempted.

(*i*) The partial oxidation of $[NEt_4][M(mnt)_2]$ dissolved in acetonitrile was attempted using 0.1 mol equiv. of iodine. The solution was warmed for 6 h and then allowed to cool before the addition of [mb]Cl in acetonitrile. Analyses of the products showed them to be either ill defined or the simple salt

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† *Non-S.I. unit employed:* eV ≈ 1.60×10^{-19} J.

($x = 1$). No products corresponding to a non-stoicheiometric compound could be characterised.

(*ii*) Aerial oxidation of the acid $H_2[Pt(mnt)_2]$ in the presence of Li^+ ions was originally used to produce $Li_{0.82}[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$.[1] This method was repeated using $[mb]^+$ instead of Li^+ ions in H_2O and H_2O–Me_2CO (3 : 7 v/v) mixture. The platinum salt gave small black crystals of ill defined composition after 3 months. The palladium salt is not susceptible to aerial oxidation.

(*iii*) $Li_{0.82}[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$ dissolved in acetonitrile was added to 0.8 mol equiv. of $[mb]^+$ in acetonitrile and the mixture allowed to evaporate slowly. A brown-black solid was obtained which, on repeated recrystallisation, analysed as the simple 1 : 1 mb salt.

(*iv*) The electrochemical preparation of a partially oxidised salt starting from $[NEt_4]_n[M(mnt)_2]$ (n = 1 or 2) was attempted in acetonitrile, CH_2Cl_2, or Me_2CO. Both potentiostatic and galvostatic methods were used with platinum-wire and -foil electrodes. We concentrated on constant-current experiments as these had proved most productive in the past.[9] Currents of between 1 and 100 μA were employed over periods ranging from 1 day to 8 weeks at 25 °C. These experiments gave a clean, microcrystalline product of the simple 1 : 1 salt, irrespective of the oxidation state of the starting material.

Physical Measurements.—The room-temperature d.c. conductivity (σ) was measured using a two-probe technique on compacted discs pressed at 1.5 tons (*ca.* 1.5 Mg) pressure. Measurements were made using both colloidal graphite and colloidal silver to attach gold wires to the sample. Measurements were made at currents below 10 nA and voltages less than 10 V. The single-crystal measurements were made using a four-probe d.c. technique and colloidal graphite contacts. Computer-assisted variable-temperature d.c. conductivity measurements were performed between 310 and 240 K on $[mb][Pt(mnt)_2]$ crystals. The temperature was cycled in steps of ± 2 K.

Reflectance spectra were recorded on powdered samples using a Beckman DK-2A ratio recording spectrophotometer, fitted with a standard reflectance attachment, in the range 4 000—29 000 cm^{-1}.

Results and Discussion

The d.c. electrical conductivities (σ) of compressed pellets of the simple 2 : 1 and 1 : 1 salts are given in Table 2. The range of σ values obtained are shown for the three or more separate discs measured. In general, differences of up to two orders of magnitude were observed on different pellets of the same salt. The values obtained for $[mb]_2[Ni(mnt)_2]$ are in reasonable agreement with the previously reported value.[4] The value of σ for $[mb][Ni(mnt)_2]$ shows the greatest range, with the majority of the samples having $\sigma \approx 10^{-9}$ to 10^{-10} Ω^{-1} cm^{-1}. This is two orders of magnitude less than that previously reported.[4] One disc, however, exhibited a conductivity of 3×10^{-5} Ω^{-1} cm^{-1}. Similar diverse results have been observed for $[mb]_2[Fe(mnt)_3]$ prepared from different solvent mixtures.[4]

The room-temperature four-probe d.c. conductivity measurements on single crystals of $[mb][Pt(mnt)_2]$ were stable and reproducible, $(1.00 \pm 0.05) \times 10^{-5}$ Ω^{-1} cm^{-1}, for three samples of differing dimensions. The crystals were rectangular wafers in shape (3.0 × 0.20 × 0.07 mm) and the conductivity was measured along the longest edge.

The crystals exhibited semiconductor behaviour over the temperature range 240—310 K with an activation energy of 238 meV. This is similar to that observed for compressed powders of $[mb][Ni(mnt)_2]$ (207 meV). These are typical of activated semiconductors showing 'hopping' (redox) conductivities.[4] The results in Table 2 for the Pd and Pt salts show that the 1 : 1 salts are more conducting than the 2 : 1 salts by a factor of *ca.* 10^2. This is in agreement with results obtained for salts of these anions with other cations. The higher conductivity observed for the nickel monoanion salt has been ascribed to the ease of disproportionation of monoanion compared with that of the dianion salt.[4]

Table 2. Electrical conductivity data [a]

Compound	σ/Ω^{-1} cm^{-1}
$[mb]_2[Ni(mnt)_2]$	4.5×10^{-10} to 3×10^{-8} (4) $[1 \times 10^{-9}]$ [b]
$[mb]_2[Pd(mnt)_2]$	$<10^{-12}$ to 5×10^{-10} (5)
$[mb]_2[Pt(mnt)_2]$	7×10^{-10} to 2×10^{-9} (3)
$[mb]_2[Cu(mnt)_2]$	$<10^{-12}$ (3)
$[mb][Ni(mnt)_2]$	3×10^{-10} to 3×10^{-5} (4) $[6 \times 10^{-7}]$ [b]
$[mb][Pd(mnt)_2]$	1×10^{-10} to 1×10^{-8} (5)
$[mb][Pt(mnt)_2]$	5×10^{-10} to 2×10^{-6} (8) $[1 \times 10^{-5}]$ [c]
$[mb][Cu(mnt)_2]$	$<10^{-12}$ (3)

[a] The number of discs examined is shown in parentheses. [b] Value from ref. 4. [c] Single-crystal measurement.

In these simple salts the conduction pathway could involve the $[mb]^+$ cations only, the metal dithiolate anions only, or a combination of both ions. A dominant conduction pathway is not apparent from the results obtained. The values of σ are, however, similar to those found for the anions in the presence of bulky cations such as $[NEt_4]^+$.[4,10] The difference in σ between the di- and mono-anions is also reminiscent of salts with conduction through the dithiolate anions. The conductivity of $[mb]^+Cl^-$ has been reported as 10^{-6} Ω^{-1} cm^{-1}, somewhat higher than that of the compounds reported here.[4] Thus the evidence would suggest that conduction is *via* the dithiolate anions rather than the $[mb]^+$ cations. There is no evidence that the combination of redox active cation and dithiolate anion is leading to enhanced conductivity compared with the parent materials. This is substantiated by studies of the diffuse reflectance spectra of the salts which appear to be a superimposition of the spectra of the constituent ions. No additional low-frequency absorption bands were observed to indicate heteronuclear interaction.

All attempts to produce highly conducting non-integral oxidation state systems involving $[mb]^+$ as the cation were unsuccessful. This may be due to the size of the cation, although the separation between mb molecules in [mb]Cl and [mb][SCN] is only 3.38 Å, less than that observed for the intra-stack distance in $Li_{0.82}[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$ (3.64 Å).[3,11] More importantly it may be the absence of a hydrated cation which in $Li_{0.82}[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$ helps to stabilise a two-dimensional sheet network, *via* hydrogen bonding, thus facilitating strong S–S binding between adjacent stacks of $[Pt(mnt)_2]$ anions.[3]

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