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THE CHEMISTRY AND SOLID STATE PROPERTIES OF NICKEL, PALLADIUM AND PLATINUM BIS(MALEONITRILEDITHIOLATE) COMPOUNDS*

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CONTENTS

A. INTRODUCTION

There are many areas in chemistry that have recently grown in importance which are not strictly the realm of the chemist. Examples of these can be found in the fields of bioinorganic and organometallic chemistry. Another

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*Chemical Abstracts' name for the maleonitriledithiolate compounds is bis[2,3-dimercapto-2-butanedinitrilato-2-S,S^1].

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example of this has been the growing interest of physicists and chemists in low-dimensional solids and pseudo one-dimensional systems. These materials have potential technological applications in the electronics industry; for example, various organic molecules have applications as non-linear optical materials in optical waveguides for phase matching. Various low-dimensional materials are also used as ionic conductors in solid state batteries.

There is an advantage in studying low-dimensional rather than conventional three-dimensional materials in that theoretical models can be tested more readily when applied to one-dimensional systems. There are many quasi one-dimensional materials which are semiconductors and some of these are of interest due to their unusual magnetic properties. The relationship of magnetic properties to structure is of great importance in inorganic chemistry, the ramifications of which apply to both chemists and physicists alike. These are apparent in cluster systems as well as metal atom chain systems.

Examples of compounds containing molecular stacks that have low-dimensional properties are the organic charge transfer complexes which are known to exhibit unusual solid state properties. They have been found to show metallic properties with the conduction pathway through stacked near planar organic molecules. A series of non-metallic or semiconductor organic charge transfer complexes are also known; high electrical conductivity is not observed in these compounds due to a combination of structural and electronic properties.

This series of compounds has been discussed in detail in various reviews notably by McCleverty in 1968 [1], Eisenberg in 1970 [2], Burns and McAuliffe in 1979 [3]. These compounds also have applications in analytical chemistry [4,5] as well as in solid state and photochemistry.

High electrical conductivity has been observed in the partially oxidised tetracyanoplatinates, e.g., $K_2[Pt(CN)_4]Br_{0.3}\cdot 3.2H_2O$ (KCP(Br)) [6], and the bis(oxalato)platinates, e.g., $K_{1.62}[Pt(C_2O_4)_2]\cdot 2H_2O$ (α-KOP) [7]. These compounds were first discovered in the last century and have been well characterised [8,9]. They have high electrical conductivity which is due to the overlap of the platinum $5d_{z^2}$ orbitals and have close Pt–Pt distances which are observed in the metal atom chain direction and approach that observed in platinum metal. Steric hindrance of the ligands is minimised as the stacking of the planar anions is staggered with respect to the adjacent anion in the stack. There is a large Pt–Pt distance between the stacks which gives rise to a high degree of anisotropy in the crystals. The 1,2-dithiolene ligand is similar to the oxalate ligand and has advantages as the R groups can be H, CH_3, ethyl, phenyl, CF_3, CN or $(CS_3)_{0.5}$, etc. In 1981 a new one-dimensional metal $Li_{0.82}(H_3O^+)_{0.33}[Pt(S_2C_2(CN)_2)_2]\cdot 1.67H_2O$ (α-LiPtmnt) was discovered, the first one-dimensional metal prepared based solely on the metal dithiolene anion [10]. Previously electrically conducting metal dithiolene complexes involved large charge transfer cations such as in (perylene)$_2$[Pt($S_2C_2(CN)_2)_2$] [11]. More recently the semimetal $Cs_{0.83}$-[Pd($S_2C_2(CN)_2)_2$]·0.5H_2O (CsPdmnt) was found to behave as a metal under pressure (12 kbar) down to 30 K owing to its extensive two dimensionality [12]. The first organometallic compound TTF[Ni(dmit)$_2$]$_2$ discovered that behaved as a superconductor under a pressure of 7 kbar at 1.6 K [13] was one based on a metal 1,2-dithiolene stack structure, which possessed a three-dimensional structure with integrating S–S interactions less than the van der Waals radius of 3.60 Å [14]. There has also been a preliminary report of superconductivity in (BEDT-TTF)[Ni($S_2C_2(CN)_2)_2$] [15]. Alvarez et al. [16] have recently studied the stacking in the transition metal dithiolene and tetrathiolates by quantitative molecular orbital and band structure calculations, and have correlated the size of the counteranion with the already reported stacked structures. Interest has been focused on solid state physics after the recent discovery of high temperature superconductivity (100 K) in the lanthanum and yttrium barium copper oxide ceramics (MBaCuO$_4$, M = La and Y) [17] for which the Nobel Prize in Physics was awarded in 1987.

This review is concerned with the chemistry and solid state properties of nickel, palladium and platinum bis(maleonitriledithiolate) compounds.

B. TRANSITION METAL BIS(DITHIOLENE) COMPLEXES

The most studied transition metal bis(dithiolene) complexes are the bis(1,2-dithiolenes) which form a five membered ring with the transition metal whilst the bis(1,1-dithiolenes) and the bis(1,3-dithiolenes) form four- and six-membered rings respectively with the transition metals. This produces a degree of strain in the 1,1- and the 1,3-dithiolene complexes and was confirmed by a molecular orbital treatment by Schrauzer [18]. The 1,2-dithiolenes form square coplanar complexes with transition metals having a d^8 configuration such as nickel(II), palladium(II) and platinum(II).

Bähr and Schleitzer [19] prepared disodium maleonitriledithiolate (disodium dicyanoethylenedithiolate) $Na_2S_2C_2(CN)_2$ by the reaction of carbon disulphide with sodium cyanide in *N,N'*-dimethylformamide, producing a stable intermediate which was recrystallised in 2-methyl-1-propanol. This intermediate was dimerised by the addition of a large volume of water which precipitated sulphur. The reaction was complete after 48 h and the product was purified by recrystallisation from ethanol. They had prepared some transition metal salts of the ligand but only to prove that the ligand was the *cis* form.

Gray et al. [20] used the maleonitriledithiolate ligand to react with divalent transition metal ions to produce the bis(1,2-dicyanoethylenedithiolate)metalate(-2) complex. The complexes were isolated as crystals of the tetraalkylammonium salts. Schrauzer and Mayweg [21] had previously reported the preparation of another 1,2-dithiolate complex with a divalent transition metal ion, namely $[Ni(S_2C_2(C_6H_5)_2)_2]^0$, as black crystals. The complexes prepared by Williams et al. [22] were nickel and palladium 1,2-dithiolene complexes with $R = Ph$, CF_3 and CN; these were the first planar four coordinate complexes of the group eight metals found to be paramagnetic.

C. REDOX PROPERTIES OF THE METAL 1,2-DITHIOLENES

Williams et al. [22] found that the $[M(S_2C_2(R)_2]^{2-}$ and the neutral $[M(S_2C_2(R)_2]^0$ complexes were related by a reversible electron transfer reaction. Oxidation and reduction of the 1,2-dithiolene complexes occur in discrete steps. Oxidation states 1+ to 3− for $[M(S_2C_2(CN)_2)_2]^{x-}$ have been reported. The extremes were only found in solution and were detected by polarography [23].

Polarographic studies by Davison and co-workers [24,25] have shown that the ease of reduction in solution varies with the R substituent in the order $CN > CF_3 > C_6H_5 > H$ for the nickel 1,2-dithiolene complexes and $R = CN > CF_3$ for the remaining 1,2-dithiolene complexes. It is possible to oxidise the metal 1,2-dithiolene dianion species where $R = H$, C_6H_5, CF_3 and CN by aerial oxidation. Metal 1,2-dithiolenes usually occur as the neutral species when the substituents are $R = H$, C_6H_5 and CF_3. The complex $[Ni(S_2C_2(CF_3)_2)_2]^0$ can oxidise $[M(S_2C_2(CN)_2)_2]^{2-}$ compounds to the monoanion, which can then be separated as the tetraalkylammonium complexes of $[M(S_2C_2(CN)_2)_2]^-$ as they are only sparingly soluble in dichloromethane whereas the $[Ni(S_2C_2(CF_3)_2)_2]^-$ complexes are very soluble. The $[M(S_2C_2(CN)_2)_2]^{2-}$ complexes are readily oxidised by iodine in dimethyl sulphoxide.

The preparation of the monoanion has to be carried out quickly with rapid precipitation by the addition of $R_4N^+Br^-$ in dry ethanol in order to prepare high purity compounds [24], especially the palladium compounds which are solvent sensitive. There is also a danger of contamination with the iodine which has been found in the monoanion complex [26]. The reduction of the $[M(S_2C_2(CN)_2)_2]^{x-}$ complexes ($M = Ni$, Pd and Pt; $x = 1$, 2 and 3) has been studied by cyclic voltammetry and by polarography [27]. The visible spectrum of a green solution of $[Ni(S_2C_2(CN)_2)_2]^{3-}$ has been studied by Mines and Geiger [28] together with the ESR of a frozen solution of 1,2-dimethoxyethane at −100°C.

The electrochemistry of $[Ni(S_2C_2(CN)_2)_2]^{x-}$ ($x = 1$ or 2) on a platinum electrode has been studied in acetonitrile [29] in order to establish the diffusion coefficient and mobility of the anions.

D. SPECTROSCOPY AND PHOTOCHEMISTRY OF THE BIS(MALEONITRILEDITHIOLATE) COMPLEXES

There are many factors that accelerate the rate of chemical reactions: these include heat, sound, pressure, light and catalysts. There are also chemical reactions that can only occur when the reactants are irradiated with visible or UV radiation. Examples of these reactions are found in inorganic, organic and polymer chemistry. This section of the review includes an overview of the IR and UV-visible spectra of the nickel, palladium and platinum bis(maleonitriledithiolate) compounds, and their photochemical application.

The photochemistry of the 1,2-dithiolene complexes has received a great deal of attention, particularly in recent years. This is due in part to their interesting redox properties, which are in turn determined by the metal's oxidation state and the delocalisation of the charge in the dithiolene ligand. The delocalisation of charge is affected by the R substituent and dithiolene ligands bearing different R groups have been prepared and studied as complexes. The research in photochemistry and spectroscopy has led to their application as new devices and related products.

The IR spectra of a range of tetraethylammonium bis(1,2-maleonitriledithiolate) Ni, Pd and Pt complexes have been recorded [30]. Assignments for the Ni–S stretching and bending modes were made by examining the complexes with the two isotopes ^{58}Ni and ^{62}Ni [31]. The IR spectra of the $K[Ni(S_2C_2(CN)_2)_2]\cdot H_2O$ and $K[Pt(S_2C_2(CN_2)_2]\cdot H_2O$ salts have been recorded and a much broader signal for the $C{=}C$ stretching mode was assumed to be due to a stack structure containing anion dimers in the Pt complex [32]. IR absorbing composites of hexadecyltrimethylammonium bis(1,2-maleonitriledithiolate)nickelate(II) and other 1,2-dithiolene complexes have been reported [33]. The complexes absorb near-IR and far-IR radiation, but it does not prevent visible radiation from passing through the material.

Resonance-raman and low temperature (80 K) absorption spectra have been recorded on the bistetraethylammonium bis(maleonitriledithiolene)metalate complexes [34].

The UV-visible spectra of the bis(1,2-maleonitriledithiolate) complexes have been studied extensively [35,36]. The reflectance spectra of one-dimensional and quasi one-dimensional materials usually have a high absorbance throughout the visible region. The optical properties of these materials have often been investigated by research workers when studying the one-dimensional metal atom chain compounds and charge transfer complexes.

The photooxidation of the dianion complexes $[M(S_2C_2(CN)_2)_2]^{x-}$ (M = Ni, Pd and Pt; $x = 2$) and monoanion complexes (M = Ni; $x = 1$) have been studied in chloroform at 300 and 350 nm [37]. An increase in the absorbance at 845, 1111 and 855 nm was observed for the Ni, Pd and Pt complexes respectively [35]. The excited state of tris(2,2′-bipyridine) ruthenium(II) ($[Ru(bpy)_3]^{2+}$) complexes produced by 1,2-dithiolene complexes has been examined by Chiorboli et al. [38] and earlier by Frank and Rau [39]. The bis(1,2-maleonitriledithiolate) complexes, when dissolved in a water/tetrahydrofuran solution, have been shown to produce hydrogen gas under UV irradiation [40–42]. However, the mechanism of the photooxidation of the $[Ni(S_2C_2(CN)_2)_2]^{2-}$ complex has been disputed by Dooley and Patterson [43] who studied the photooxidation in a chloroform/methyl cyanide solution. They concluded that the redox properties of the complexes are mainly associated with the ligand rather than the metal and this is supported by molecular orbital calculations. This may be of some significance when trying to understand the mechanism of the photooxidation process. The photochemistry has been examined on ion-exchange films and the quenching by water has also been studied [35,44,45]. A composite coating of a cyanine dye, nitrocellulose and $K_2[Ni(S_2C_2(CN)_2)_2]$ on a suitable substrate can be used for high quality laser recording discs [46]. The conversion of light at 480 nm to electricity can be achieved by using a coating of $[N(C_2H_5)_4][Ni(S_2C_2(CN)_2)_2]$ on a platinum electrode solution evaporated onto the surface from a solution of methyl cyanide in an aqueous electrolyte [47]. Optical studies using polarised spectra from $[N(C_4H_9)_4]_2[Ni(S_2C_2(CN)_2)_2]$ [48] (parallel and perpendicular to the electric vector) have helped to assign the electronic spectra further.

Güntner and Gliemann [49] have recently made a similar study on single crystals of $[N(C_4H_9)_4]_2[Pt(S_2C_2(CN)_2)_2]$. Their work suggests that the LUMO of $[Pt(S_2C_2(CN)_2)_2]^{2-}$ has π^* (antibonding orbitals) rather than the metals d_{xy} orbitals as in the $[Ni(S_2C_2(CN)_2)_2]^{2-}$ case [50].

There are many patents covering a range of 1,2-dithiolenes which are used in optical recording [51–56] and as bar codes [57].

E. INTRAMOLECULAR METAL LIGAND BONDING IN THE BIS(MALEONITRILEDITHIOLATE) COMPLEXES

The nature of the metal ligand bonding in the metal dithiolenes has been studied by many workers using various computational methods. There are four ligand π orbitals which interact with the metal's atomic orbitals (the dithiolene ligand orbitals are shown in Fig. 1). Alvarez et al. [16] have

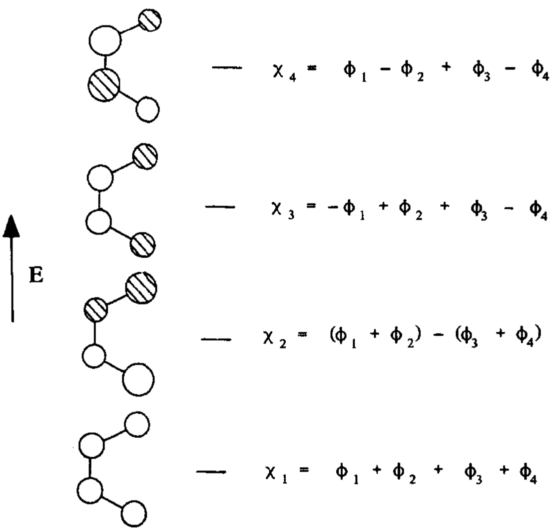

Fig. 1. The 1,2-dithiolene *p* orbitals which form the *π* MOs that are available for bonding to the metal's *d* orbitals.

calculated the *π* character in the orbitals as $\chi 1$ 54%, $\chi 2$ 89% and $\chi 3$ 46% located on the two sulphur atoms, which showed that $\chi 2$ has more *π* character than the other orbitals.

The *π* orbital combinations are now able to interact with the metal's *d* orbitals provided they are of the correct symmetry and are also close in energy. Schrauzer and Mayweg [50] used an extended Hückel method and placed the 3*d* level between the $\chi 2$ and $\chi 3$ energy levels of the ligand when calculating the MO diagram for $[Ni(S_2C_2H_2)_2]^{2-}$ complex. However, there have been more recent studies on the same complex using ab initio methods [58–60] which suggest that the *π* orbitals lie above the metals 3*d* orbitals, indicating that the HOMO contains almost entirely ligand orbital character as shown in Fig. 2.

The theoretical predictions are supported by IR spectral evidence which shows an increase in the force constant of the C═C bond and a decrease in the force constants of the C—S and M—S bond in going from the neutral to the mono- and dianionic dithiolene complex [31] respectively. The effect of changing the R group from H to CN has increased the total number of electrons from 16 to 64 thus making an ab initio treatment of the dicyanoethylenedithiolene ligand too big a problem for computers that are available today. However, semiempirical methods have been employed [61–64]. The effect of extending the *π* system by the inclusion of electron withdrawing groups stabilises the compound and makes it less reactive. In terms of the

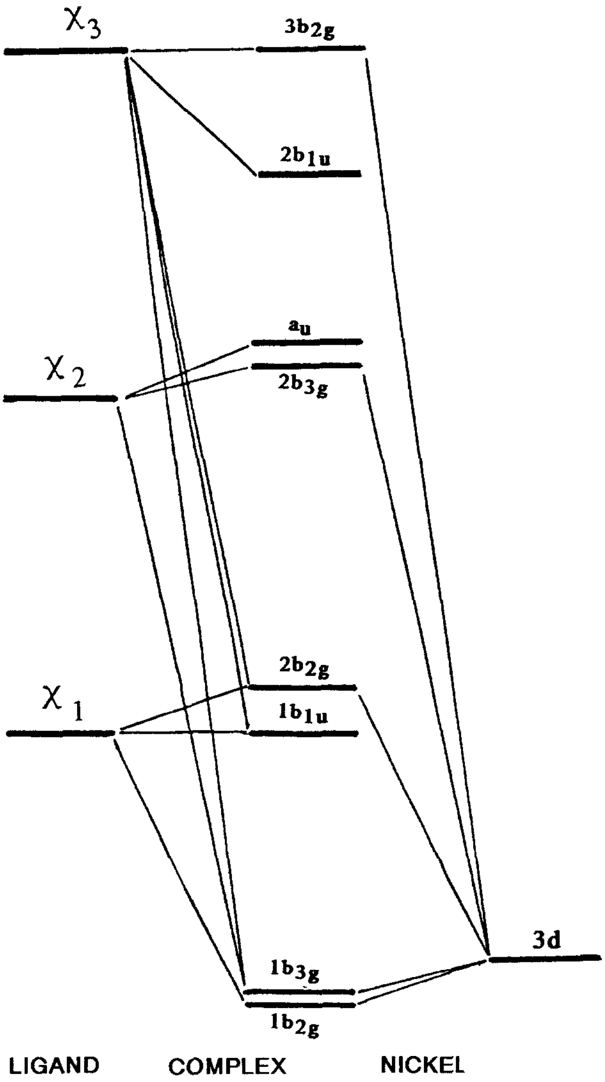

Fig. 2. The energy level diagram of $[Ni(S_2C_2H_2)_2]^{2-}$.

energy level diagram, the π orbitals of the dicyanoethylenedithiolene ligand are lower in energy than the ethylenedithiolene ligand and hence the HOMO of the complex has more metal orbital character (shown in Fig. 3) than that of the bis(ethylenedithiolato)nickelate(2−) complex with which most of the molecular orbital calculations have been concerned.

Zubenko et al. [65] have examined the effects on the general structure with the mixed dithiolene ligands by using a self consistent field, MO LCAO method.

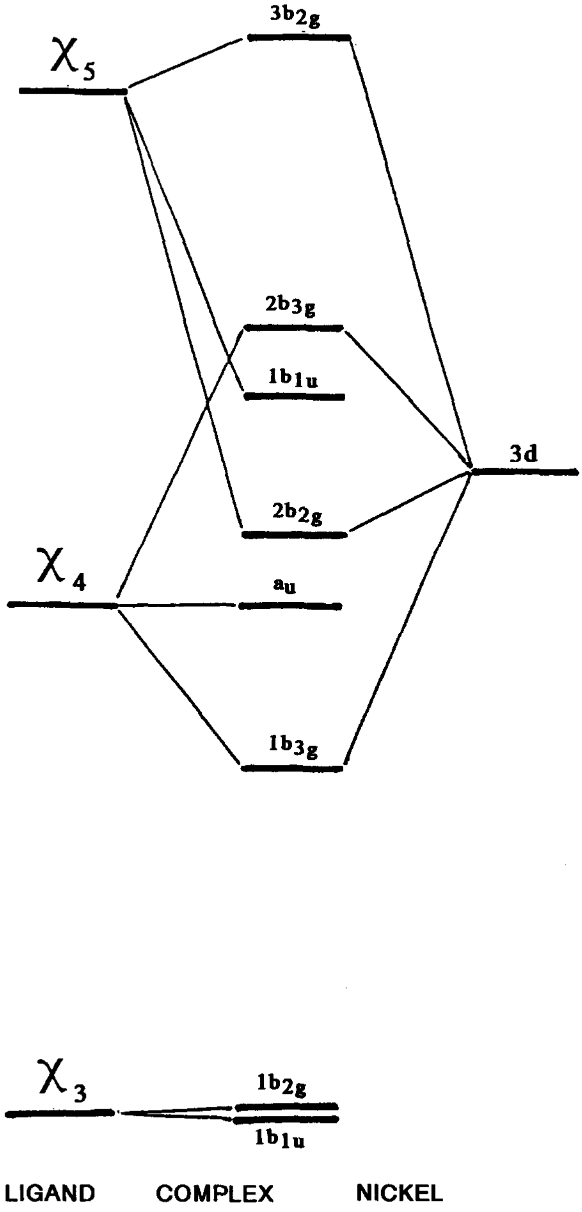

Fig. 3. The energy level diagram of $[Ni(S_2C_2(CN)_2)_2]^{2-}$.

F. THE EFFECT OF CHANGING THE CENTRAL METAL IN THE BIS(MALEONITRILEDITHIOLATE) COMPLEXES

The effect of changing the central metal from nickel to palladium or platinum makes very little difference to the reactivity of the ethylenedithiolene complex in spite of the increase in the size of the spatial envelope in going from the 3*d* to 4*d* through to the 5*d* orbitals. However, in the dicyanoethylenedithiolene complex the HOMO has more metal character and greater differences in the reactivity may be expected. Recently the charge distribution in $[M(S_2C_2(CN_2)_2]^{n-}$ complexes (where M = Ni and Pt; $n=2$, 1 and 0), has been calculated by an extended Hückel calculation which has been optimised for charge distribution [66] (see Table 1).

This investigation is still in its early stages and possibly the most interesting study would be one on $[Pd(S_2C_2(CN)_2)_2]^{n-}$ ($n=2$, 1 and 0) for which it is known that the Pd–S orbital overlap is greater than for either the Pt–S or Ni–S case [67]. The range of charge on the platinum atom is 0.46+ for the dianion to 0.61+ on the neutral complex compared with values for the nickel complex of 0.66+ to 0.76+. There is very little difference between the nickel and platinum complexes except that the charge on Pt is less than that on Ni in all of them.

There have been, however, ambiguities in the electron counting and oxidation state of the central metal in 1,2-dithiolene metal complexes. The dithiolene is a non-innocent ligand that can either be neutral or dianionic [50] (Fig. 4).

TABLE 1

Extended Hückel total charge density distribution in $[Pt(S_2C_2(CN)_2)_2]^{n-}$ and $[Ni(S_2C_2(CN)_2)_2]^{n-}$ ($n=2$, 1 and 0) [66][a]

Atom	Complex		
	$[M(mnt)_2]^0$	$[M(mnt)_2]^-$	$[M(mnt)_2]^{2-}$
M = Pt			
Pt	+0.609[b]	+0.542	+0.464
S	−0.165	−0.354	−0.532
C(1)[c]	+0.131	+0.102	+0.067
C(2)[d]	+0.122	+0.121	+0.118
N	−0.240	−0.254	−0.270
M = Ni			
Ni	+0.764[b]	+0.718	+0.660
S	−0.165	−0.359	−0.541
C(1)[c]	+0.106	+0.077	+0.042
C(2)[d]	+0.122	+0.111	+0.108
N	−0.243	−0.258	−0.275

[a] Sulphur *p* coulomb = −12 eV; Ni *d* coulomb = −13.49 eV; Pt *d* coulomb = −12.59 eV. [b] Estimated by subtracting the electron density in HOMO of the monoanion from total charge density of the monoanion. [c] (1) Ethylene carbon atom. [d] (2) Cyano carbon atom.

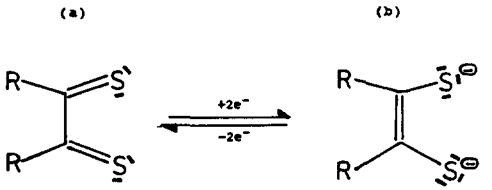

Fig. 4. The resonance structure of (a) the neutral butadienoid and (b) the dianionic dithiolene forms.

These two forms differ in the number of π electrons, the neutral butadienoid case having four π electrons and the dianion six. Molecular orbital calculations discussed earlier indicate that the electronic structure of the metal–dithiolene has three mainly dithiolene based π orbitals which are filled for the dithiolenes. This is consistent with a dianionic dithiolene resonance structure (b) rather than the neutral butadienoid resonance structure (a). Therefore in most complexes, by using rules of valency, it is easy to assign a formal oxidation state to the metal. However, one should always bear in mind the essential ambiguity of any oxidation state that is assigned (Fig. 5).

The formal oxidation states on the metal are 4+, 3+ and 2+ for the dianion, monoanion and neutral species respectively. However, the charge is delocalised over the entire molecule in the molecule orbital.

The electrons that are in the HOMO of the complex are distributed between the ligand and the metal. This is in turn dependent upon the R groups and their effect is shown in Table 2.

Various ESCA studies have been carried out on the maleonitriledithiolate complexes in order to establish the charge distribution [68,69]. A study of the anisotropy of the nickel dithiolenes has been carried out using double electron–electron resonance in a mixture of dimethylformamide and chloroform at 130–180 K [70].

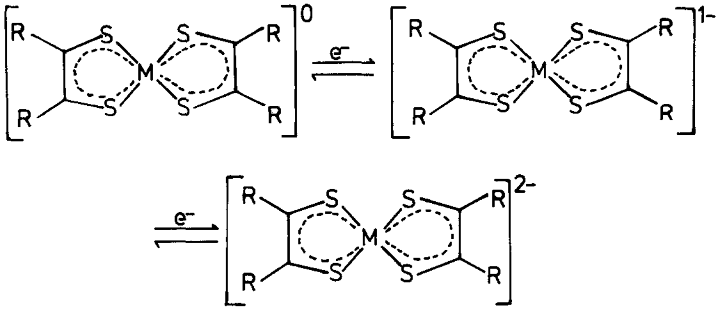

Fig. 5. The neutral, monoanion and dianion 1,2-dithiolene complexes.

TABLE 2

The charge density of the nickel 1,2-dithiolene complexes with various R groups [31]

	H	Ph	CF_3	CN
Metal electron density	0.06	0.23	0.43	0.38
Ligand electron density	0.96	0.77	0.57	0.62

G. STRUCTURAL STUDIES ON NICKEL, PALLADIUM AND PLATINUM BIS(MALEONITRILEDITHIOLATE) COMPLEXES

(i) The $[M(S_2C_2(CN)_2)_2]^{2-}$ dianion complexes with small countercations

It has been shown that the $[Ni(S_2C_2(CN)_2)_2]^{2-}$ salts exhibit absorptions at higher energies than most of the square coplanar nickel complexes [71]. More recently Vogler and Kunkely [72] have reported the reflectance spectra of the $[Ni(tim)]^{2+}[M(S_2C_2(CN)_2)_2]^{2-}$ (tim = 2,3,9,10-tetramethyl-1,4,8,11-tetraazocyclotetradeca-1,3,8,10-tetraene; M = Ni, Pd and Pt) which has an intense absorption band at 840 nm for the nickel complex due to an outer sphere ligand charge transfer transition from the anion to the cations. However the reflectance spectra of all the small cations $[M(S_2C_2(CN)_2)_2]^{2-}$ (M = Ni, Pd and Pt; small cation = NH_4^+, Rb^+, K^+, Cs^+, Mg^{2+} and Ca^{2+} compared to that of $[N(C_4H_9)_4]^+$) complexes have an intense broad band at 820–860 nm presumably due to anion–anion interactions [73].

The crystal structure of $Rb_2[Ni(S_2C_2(CN)_2)_2]\cdot H_2O$ has recently been determined as having an orthorhombic structure with a space group *Pbcn* with $a = 13.513(2)$, $b = 6.850(1)$, $c = 16.651(2)$ Å, $Z = 4$ [74]. The intramolecular stack distances between anions is 6.8 Å which is a great deal less than the distances of 8.0 Å and 9.8 Å reported for the crystal structure of $[N(CH_3)_4]_2[Ni(S_2C_2(CN)_2)_2]$ [75] and $[N(C_4H_9)_4]_2[Ni(S_2C_2(CN)_2)_2]$ [76].

(ii) The $[M(S_2C_2(CN)_2)_2]^-$ monoanion complexes with small countercations

The monoanion complexes with small countercations can be split into three groups.

(a) Non-integral oxidation state compounds comparable to the tetracyanoplatinate and bis(oxalate)platinate complexes [6,7], e.g., $Li_{0.82}(H_3O)_{0.33}[Pt(S_2C_2(CN)_2)_2]\cdot 1.67H_2O$ (α-LiPtmnt) and $Cs_{0.83}[Pd(S_2C_2(CN)_2)_2]\cdot 0.5H_2O$ (CsPdmnt).

(b) Integral oxidation state compounds which are the stoichiometric monoanion salts, many of which have unusual solid state properties.

(c) Compounds of simple stoichiometry but different from 1:1 and possibly similar to that found for $Li_{0.5}[Pt(S_2C_2(CN)_2)_2]\cdot 2H_2O$ (β-LiPtmnt). These have been found to have a tetrameric Pt–Pt metal atom chain system and this results in semiconductor behaviour [77].

Recently a series of monoanion salts have been prepared and studied for $[M(S_2C_2(CN)_2)_2]^-$ (where M = Ni, Pd and Pt) with the small countercations (Na^+, K^+, Rb^+, Cs^+ and NH_4^+). The solid state properties and crystal structures of these nickel, palladium and platinum compounds are summarised in Tables 3 and 4.

One of the most significant compounds included in this series with small countercations is the semimetal $Cs_{0.83}[Pd(S_2C_2(CN)_2)_2]\cdot 0.5H_2O$ (CsPdmnt) which has a high room temperature conductivity of around $2–11\ \Omega^{-1}\ cm^{-1}$ and an anisotropy of around 8. The temperature dependence is as a narrow band semiconductor, $\Delta E = 60–50$ meV in the range 310–80 K. The high electrical conductivity and low anisotropy can be explained by the short S–S interactions observed in the crystal structure of CsPdmnt. The crystal structure of CsPdmnt is shown in Fig. 6, viewed down the *b* axis. All cations and water molecules are omitted with the short S–S distances shown.

The pressure dependence conductivity of CsPdmnt has been measured along the *a* axis and evidence of two transitions was observed; one at around 240 K and the other at 120 K [12]. The activation energies of the semiconducting regions are gradually suppressed by increasing pressure and disappear at 5.2 and 7.4 kbar respectively. The application of pressure turns the compound into a metal with metallic behaviour persisting down to 30 K at 12.1 kbar [12] and 1.2 K at 21 kbar as shown in Fig. 7 [85]. At low temperatures at 12.1 kbar the resistance of the crystal rises very slowly to $10\ \Omega^{-1}\ cm^{-1}$ at 1.4 K. Unfortunately the crystals of CsPdmnt failed to become a superconductor.

The electrical properties of $Li_{0.82}[H_3O^+]_{0.33}[Pt(S_2C_2(CN)_2)_2]\cdot 1.67H_2O$ (α-LiPtmnt) [10] are dependent upon the overlap of molecular orbitals of the entire dithiolene ligand. The crystal structure of α-LiPtmnt has been reported as triclinic $P\bar{1}$, $a = 15.596(4)$, $b = 6.410(3)$, $c = 3.639(2)$ Å, $\alpha = 100.52(9)$, $\beta = 90.75(5)$, $\gamma = 96.28(6)°$, $Z = 1$ [79] and is shown in Fig. 8.

Examination of the crystal structure of α-LiPtmnt [79] reveals that the planar $[Pt(mnt)_2]^{1.18-}$ anions are arranged in an equidistant stack with short Pt–Pt distances of 3.639 Å in the needle axis of the crystal. The single crystal electrical conductivity of α-LiPtmnt is $300–20\ \Omega^{-1}\ cm^{-1}$ (four probe measurement) in the metal atom chain direction at room temperature. The conductivity of α-LiPtmnt initially only showed a slight change in conductivity when the compound was cooled below room temperature [10]. Metallic behaviour persisted down to 200 K, below which the conductivity fell rapidly with decreasing temperature. α-LiPtmnt behaved as a semicon-

TABLE 3

The solid state properties of the monoanions and partially oxidised $[M(S_2C_2(CN)_2)_2]^{x-}$ salts (M = Ni, Pd and Pt; $X = 1$ and 1.18) [73,78]

Cation	Size (Å)	Nickel		Palladium		Platinum	
		Electrical conductivity	Magnetic properties	Electrical conductivity	Magnetic properties	Electrical conductivity	Magnetic properties
Li^+	0.68	Metallic $10\ \Omega^{-1}\ cm^{-1}$[a] [78]		Metallic $1\ \Omega^{-1}\ cm^{-1}$[a] [78]	Diamagnetic	Metallic 30–200 $\Omega^{-1}\ cm^{-1}$, T_c 213 K, 36 meV[b] [10,79]	Paramagnetic 4.5×10^{-5} emu mol^{-1} [80]
Na^+	0.98	Semiconductor $10^{-5}\ \Omega^{-1}\ cm^{-1}$, 260 ± 10 meV (300–200 K)[c]	Paramagnetic $J \approx 1000$ K[d]	Semiconductor $7 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$, 60 meV (< 100 K)[a]	Diamagnetic	Semiconductor $3.7 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$, 88 ± 5 meV, (310–200 K)[a]	Diamagnetic
K^+	1.33	Semiconductor $10^{-6}\ \Omega^{-1}\ cm^{-1}$, 345 ± 5 meV (300–250 K)[c]	Paramagnetic $J \approx 1000$ K[d]	Semiconductor $1.5 \times 10^{-1}\ \Omega^{-1}\ cm^{-1}$, 159 meV (310–100 K)[b]	Diamagnetic	Semiconductor $5.9 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$, 410 ± 5 meV (310–210 K)[a]	Diamagnetic
NH_4^+ or H_3O^+	1.43	Semiconductor $4 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$, 64 ± 5 meV (310–50 K)[b]	Paramagnetic $J = 240$ K[d]	Semiconductor $6.7 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$, 213 meV (310–190 K), 163 meV (190 K)[b]	Paramagnetic $\Delta_m = 100$ K[e]	Semiconductor $10^{-5}\ \Omega^{-1}\ cm^{-1}$, 309 ± 15 meV (310–220 K)[b]	Diamagnetic[f]
Rb^+	1.48	Semiconductor $10^{-5}\ \Omega^{-1}\ cm^{-1}$, 190 meV (310–160 K)[a]		Semiconductor $1.4 \times 10^{-1}\ \Omega^{-1}\ cm^{-1}$[b]	Diamagnetic	Semiconductor [81] $2.5 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$, 300 ± 5 meV (250 K), 240 ± 5 meV (259 K)[b]	Paramagnetic μ_{eff} 1.45 BM, Curie constant 0.26
Cs^+	1.67	Semiconductor $6 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$, 193 ± 10 meV (310–200 K) 164 ± 10 meV (200–60 K)[a] [78]	Paramagnetic $\Delta_m = 394$ K[e]	Semimetal 2–11 $\Omega^{-1}\ cm^{-1}$, 55 ± 5 meV (310–80 K)[b]	Paramagnetic $\Delta_m = 97$ K[e]	Semiconductor $1.8 \times 10^{-1}\ \Omega^{-1}\ cm^{-1}$, 192 ± 20 meV (310–130 K)[a]	Paramagnetic μ_{eff} 1.32 BM

[a] The conductivity measured on a compressed disc.

[b] The single crystal conductivity was measured by attaching four gold wire contacts using colloidal graphite.

[c] The single crystal conductivity was measured using two contacts as the crystals were too small to allow four contacts.

[d] The magnetic properties are consistent with a Heisenberg antiferromagnetic chain (J = high temperature coupling constant between adjacent anions in the stacked structure [82] Bonner Fisher activation energy).

[e] The magnetic properties can be explained by a singlet–triplet transition [83] (Δ_m = activation energy).

[f] Diamagnetic at room temperature but gradually becoming paramagnetic over a period of 40 days at 24 ± 1°C.

TABLE 4

The X-ray structure of the monoanion and partially oxidised $[M(S_2C_2(CN)_2)_2]^{x-}$ salts (M = Ni, Pd and Pt; $x = 1$ and 1.18) [73]

Cation	Size (Å)	Nickel	Palladium	Platinum
Li^+	0.68	Orthorhombic, $Z=4$ $a=11.65$, $b=31.82$, $c=3.74$ Å[a] [78]		Triclinic, $P\bar{1}$, $Z=1$ $a=15.596(4)$, $b=6.410(3)$, $c=3.639(2)$ Å[a] [79]
Na^+	0.98	Orthorhombic, $Z=4$ $a=12.30$, $b=27.72$, $c=3.77$ Å[a,c]		Triclinic $c^*=6.58$ Å[b,c]
K^+	1.33	Orthorhombic, $Z=4$ $a=12.10$, $b=28.87$, $c=3.91$ Å[a,c]	Orthorhombic *Pnam*, $Z=4$ $a=12.176$, $b=29.614$, $c=3.778$ Å[a] [86]	Triclinic $c^*=6.66$ Å[b,c] [89]
NH_4^+ or H_3O^+	1.43	Orthorhombic *Pnam*, $Z=4$ $a=12.096(4)$, $b=29.216(5)$ $c=3.918(8)$ Å[a] [84,88]	Triclinic $P\bar{1}$, $Z=2$ $a=6.724(1)$, $b=14.688(4)$, $c=7.153(4)$ Å[b] [86]	Triclinic $P\bar{1}$, $Z=2$ $a=14.699(5)$, $b=7.218(3)$, $c=6.688(3)$ Å[b] [87]
Rb^+	1.48	$c=4.01$ Å[a,c]	Orthorhombic, $Z=8$ $a=13.37$, $b=29.30$ $c=6.37$ Å[b,c]	Triclinic $P\bar{1}$, $Z=2$ $a=14.659(17)$, $b=7.179(6)$, $c=6.734(2)$ Å[b] [81]
Cs^+	1.67		Orthorhombic *Pnam*, $Z=8$ $a=13.958(2)$, $b=29.940(1)$, $c=6.511(2)$ Å[b] [85]	Triclinic $c^*=7.33$ Å[b,c]

[a] An equidistant stacked metal–metal structure.

[b] A stack structure which contains dimers of anions eclipsed with metal–metal interactions in the dimer pair.

[c] The crystal parameters and angles were measured using a Stoe–Weissenberg camera.

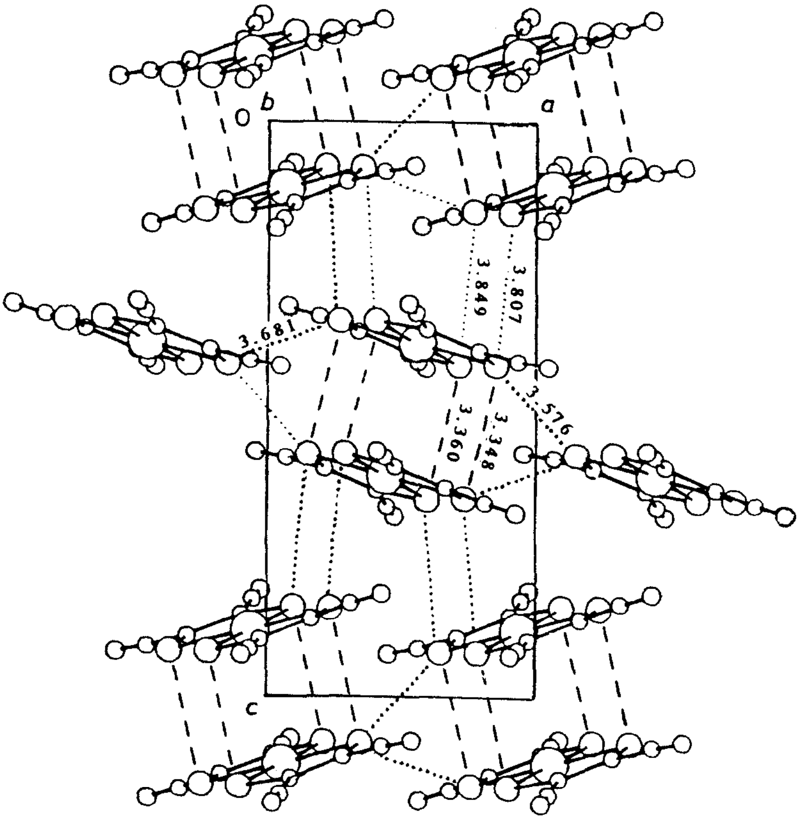

Fig. 6. The crystal structure of $Cs_{0.83}[Pd(S_2C_2(CN)_2)_2]\cdot 0.5H_2O$ viewed down the *b* axis. All cations and water molecules are omitted with the short S–S distances shown [85].

ductor below 100 K with an activation energy of 36 meV. The nature of the metal to semiconductor transition has been investigated by various techniques such as thermoelectric power, reflectance spectroscopy and low temperature structural studies [78,91,92] and is due to Peierls instability [93]. The low temperature Peierls superstructure form of a α-LiPtmnt at 153 K has been examined below the metal–semiconductor transition [92]. Applying pressure on single crystals of $Li_{0.82}[H_3O^+]_{0.33}[Pt(S_2C_2(CN)_2)_2]\cdot 1.67H_2O$ appears to lower the bandgap and at a pressure of 10 kbar, the activation energy is less than 10 meV [94] which is similar to that observed in the organic metal HMTTF-TCNQ [95].

Initially studies were only carried out on complexes with bulky counter-cations such as the tetraalkylammonium salts, $[N(CH_3)_4]^+$, $[N(C_2H_5)_4]^+$ and $[N(C_4H_9)_4]^+$ [76,96,97] or with large organic cationic salts such as *N*,*N*,*N'*,*N'*-tetramethyl-1,4-phenylenediamine cation (Wursters Blue TMPD) [98,99]. These cations formed simple salts with the monoanions and large

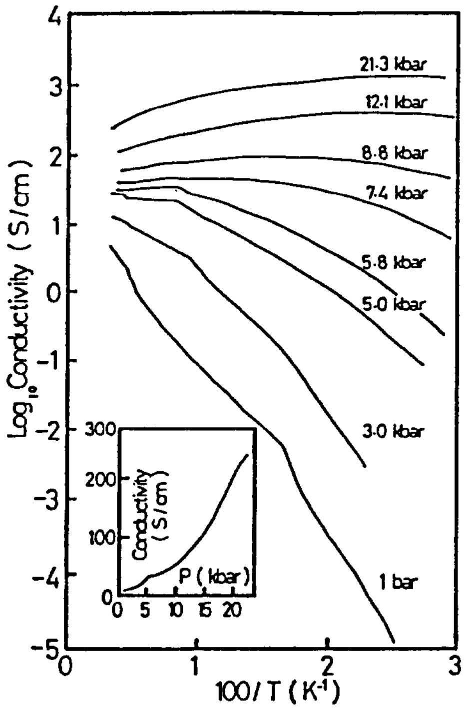

Fig. 7. The conductivity plotted against reciprocal temperature at several pressures (kbar) for CsPdmnt [90]. Insert shows the pressure dependence of the conductivity at room temperature.

high quality single crystals were easily produced. The electrical conductivities were low and in the range 10^{-6}–10^{-2} Ω^{-1} cm^{-1} [76,100]. There were, however, a few notable exceptions: these were for complexes with perylene, tetrathiafulvalene (TTF) and tetrathiatetracene (TTT), i.e., larger planar organic cations [100,101]. The electrical conductivity, however, in these compounds was found to be solely through the cations. The monoanion complexes have been shown to be considerably more conducting than the corresponding neutral or dianion complexes, and Rosseinsky and Malpas [102] have proposed that this is related to a disproportionation mode of electron transfer in the solid state. The mechanism for conduction in the monoanions and neutral 1,2-dithiolenes involves an activated hopping process similar to that in the organic crystals. Conduction occurs between dimer pairs in the stack and carrier electrons are accommodated in the LUMO of the molecule. Electrical conduction requires the generation of electrons which are then transmitted in the stack with the formation of monocations and monoanions. In the monoanion 1,2-dithiolenes conduction process, neutral and dianionic species are initially produced. Charge

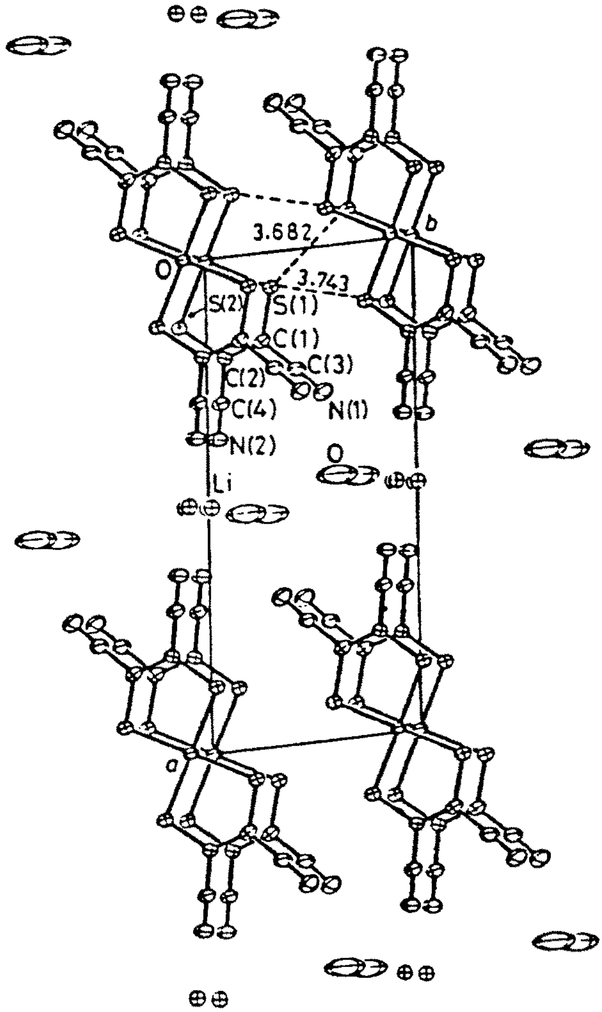

Fig. 8. The c^* axis projection of the crystal structure of $Li_{0.82}[H_3O^+]_{0.33}[Pt(S_2C_2(CN)_2)_2]\cdot 1.67H_2O$ [79].

transfer complexes such as $(perylene)_2[M(S_2C_2(CN)_2)_2]$ were however found to behave as one-dimensional solids [11,101,103,104].

Perez-Albuerne et al. [105] published a preliminary communication on the bis(1,2-dicyanoethylene-1,2-dithiolate)nickelate(1 −) and palladate(1 −) monoanions with small inorganic cations but failed to give details of the preparation and analysis. The Na^+ and NH_4^+ compounds were reported to have variable electrical conductivities which are dependent on the degree of hydration. The effect of the countercation on the electrical conductivity is small and conduction must be attributed to the transport of charge through the dithiolene anion. The $[M(S_2C_2(CN)_2)_2]^-$ (where M = Ni, Pd and Pt) salts with small inorganic countercations can be incorporated into a polymer matrix with applications in photocopying, computer disks and audio recording tapes [106]. An earlier patent describes the preparation of many complexes with large countercations and also the preparation of single crystals of $[N(C_2H_5)_4][Cu_xNi_{1-x}(S_2C_2(CN)_2)_2]$. The compounds described in the patent have applications in paints, dyes and photocopying [107].

The nickel dithiolene compounds with small countercations, summarised in Tables 3 and 4 are all believed to form equidistant stacked structures except β-$NH_4[Ni(S_2C_2(CN)_2)_2]\cdot H_2O$ and $Cs[Ni(S_2C_2(CN)_2)_2]\cdot H_2O$ which are considered to have some sort of stacked structure containing anion dimers. All these compounds were found to behave as semiconductors and the crystal structure of α-$NH_4[Ni(S_2C_2(CN)_2)_2]\cdot H_2O$ revealed that the stacking was as a Ni–Ni overlapping chain rather than a Ni–S dimerised stack anticipated by Alvarez et al. [16]. The crystal structure of α-$NH_4[Ni(S_2C_2(CN)_2)_2]\cdot H_2O$ is shown in Fig. 9 viewed down the *b* axis. Structural studies have also been carried out at low temperatures and these have shown a doubling of the *b* axis in the unit cell. The stacking, however, remains a Ni–Ni overlapping system [84].

The structural and electronic properties of the bis(1,2-dithiolene) platinate(1 −) complexes with small countercations are summarised in Tables 3 and 4. Full crystal structures have been determined on $Rb[Pt(S_2C_2(CN)_2)_2]\cdot H_2O$ [81] and $H_3O^+[Pt(S_2C_2(CN)_2)_2]\cdot H_2O$ [87]. Preliminary structural

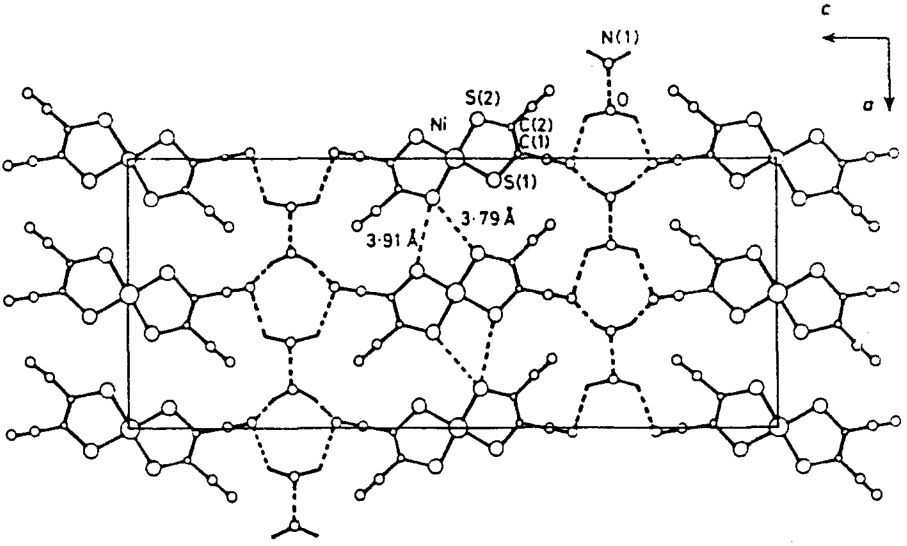

Fig. 9. The crystal structure of α-$NH_4[Ni(S_2C_2(CN)_2)_2]\cdot H_2O$ viewed down the *b* axis [84].

details have also been obtained on the Na^+, K^+ and Cs^+ compounds [70]. The crystal structures reveal that the compounds are dimers within a stack structure forming Mott–Hubbard semiconductors. These complexes possess Pt over Pt interactions within the dimerised stack structure resulting in the pairing of electrons and hence the compounds diamagnetic behaviour. The crystal structure of $H_3O^+[Pt(S_2C_2(CN)_2)_2]\cdot H_2O$ is shown in Fig. 10 viewed down the c^* axis.

The crystal structure of $[N(C_2H_5)_4][Pt(S_2C_2(CN)_2)_2]$ has also recently been resolved [87]. The structure was found to possess a dimerised stack with Pt–S interactions similar to that observed in the nickel salt [76]. These results were postulated but not anticipated by MO and band structure calculations [16].

The structural and electronic properties of the bis(1,2-dithiolene) palladate(1−) complexes with small countercations are summarised in Tables 3 and 4. There are two types of interactions that occur in the stacking axis in the crystal structures of the salts of palladium dithiolene with small countercations. In the crystal structure of $K[Pd(S_2C_2(CN)_2)_2]\cdot H_2O$ [86], the stacking interactions within the anions are via an equidistant column of Pd–Pd overlapping metal atoms in a chain similar to that in α-$NH_4[Ni(S_2C_2(CN)_2)_2]\cdot H_2O$ [84]. In the crystal structure of $NH_4[Pd(S_2C_2(CN)_2)_2]\cdot H_2O$ [86], the stacking interactions which occur

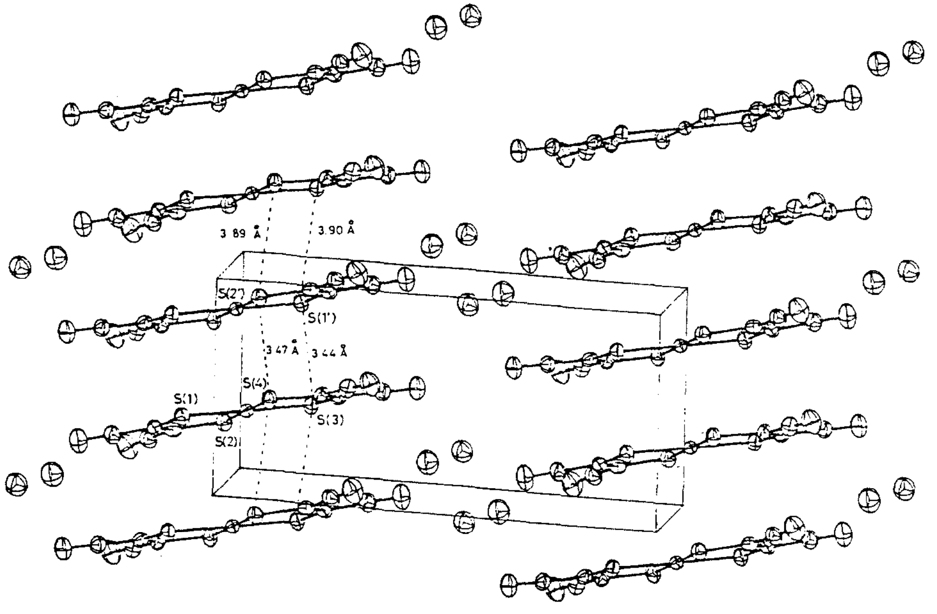

Fig. 10. The crystal structure of $H_3O^+[Pt(S_2C_2(CN)_2)_2]\cdot H_2O$ viewed down the c^* axis [87] which reveals the S–S contacts within the dimers in the stack and between dimer pairs.

between anion dimers involve a Pd–Pd eclipsed arrangement which is similar to Rb[Pt($S_2C_2(CN)_2)_2$]·H_2O [81] and H_3O^+[Pt($S_2C_2(CN)_2)_2$]·H_2O [87]. The ESR and magnetic properties of $[M(S_2C_2(CN)_2)_2]^-$ (where M = Ni, Pd and Pt) with small countercations has been studied. Details of the magnetic properties of these materials are included in Table 3 [108–111].

(iii) The charge transfer complexes with the bis(maleonitriledithiolate) acceptors

The solid state properties of the charge-transfer complexes with $[M(S_2C_2(CN)_2)_2]^{x-}$ (where M = Ni, Pd and Pt; $x = 1$ and 2) are summarised in Table 5. In these complexes, electrical interactions occur by the transfer of charge from donor to acceptor molecules within a mixed stacked structure. Torrance [112] has studied the differences between the insulating and conducting tetracyanoquinodimethane charge transfer salts and the same general ideas may have some relevance to this work on the metal bis(1,2-dithiolenes).

In 1975 Miles and Wilson [100] published an account of the solid state properties of a wide range of charge transfer complexes of $[M(S_2C_2(CN)_2)_2]^{x-}$. The charge transfer complexes such as (perylene)$_2$ $[M(S_2C_2(CN)_2)_2]$ (M = Ni, Pd and Pt) were found to behave as one-dimensional solids [11,101,103,104,113]. The (perylene)$_2$$[M(S_2C_2(CN)_2)_2]$ (M = Ni, Pd and Pt) series of compounds are the subject of much recent research. The thermoelectric power of the palladium and platinum complexes [114], their pressure dependent conductivity [115] and the crystal structure of the platinum complex [116] and palladium complex [117] have all been recently reported. The electrical transport, magnetic properties and ESR of the Pt and Pd complexes have also been studied [118,119]. Recently the crystal structures of the 1:1 salts of the organic donor tetra(methylthio) tetrathiafulvalene (TTM-TTF) and $[M(S_2C_2(CN)_2)_2]^-$ (M = Ni and Pt) were reported [120]. The crystal structures of the charge transfer complexes $(MV)^{2+}$ $[Ni(S_2C_2(CN)_2)_2]^{2-}$ (where MV = 1,1′-dimethyl-4,4′-bipyridinium, an excited photosensitiser) [121] have been resolved, respectively, as an A–B–A parallel structure and a more complicated perpendicular interpolating structure. Meier et al. [122] have recently examined the photoconductivity and conductivity of a range of methylviologen and tetraalkylammonium nickel maleonitriledithiolate complexes. The crystal and molecular structure of TTF$[Ni(S_2C_2(CN)_2)_2]$ have recently been shown to have a mixed DAD-DAD structure [123]. Renewed interest has been shown in the quasi one-dimensional compounds. The crystal structures of TMPD$^+$$[Ni(S_2C_2(CN)_2)_2]^-$ [124,127], $[Ph_4As]_2[Ni(S_2C_2(CN)_2)_2]$ [125], [*N*-methylphenazi-

TABLE 5

The electrical conductivities and thermoelectric power of the $[M(mnt)_2]^{x-}$ (M = Ni, Pd and Pt; $x = 1$ and 2) with various countercations

Compound[a]	Conductivity ($\Omega^{-1}\,cm^{-1}$)	ΔE (meV)	S (310 K) ($\mu V\,deg^{-1}$)	References
$[NEt_4]_2[Ni(mnt)_2]$	$<10^{-12}$[b] 2×10^{-12}[b]			153, 102
$[NEt_4]_2[Pt(mnt)_2]$	Approx. 10^{-10}			153
$[NEt_4][Ni(mnt)_2]$	1×10^{-8}[b] 3.4×10^{-5}[c]			105, 153
$[NEt_4][Pd(mnt)_2]$	2.5×10^{-8}[b]			105
$[NEt_4][Pt(mnt)_2]$	Approx. 10^{-8}[b]			153
$NBu_4[Ni(mnt)_2]$	10^{-10}[c]			124
$NMe_3Ph[Ni(mnt)_2]$	1.6×10^{-8}[c]			124
$[NH_4][Ni(mnt)_2]$	4×10^{-4}[b]			105
$[NH_4][Ni(mnt)_2]\cdot xH_2O$	1.0[b] 5×10^{-2}[c]			88, 105
$[NH_4][Pd(mnt)_2]\cdot xH_2O$	1.1[b]			105
$Na[Ni(mnt)_2]$	4×10^{-4}[b]			105
$Na[Ni(mnt)_2]\cdot xH_2O$	2.5×10^{-1}[b]			105
$Na[Pd(mnt)_2]\cdot xH_2O$	4×10^{-1}[b]			105
$Cu[Ni(mnt)_2]\cdot 2H_2O$	3×10^{-3}[b] 5×10^{-2}[b]			148, 150
$Cu[Pd(mnt)_2]\cdot 2H_2O$	5×10^{-6}[b]			150
$Cu[Pt(mnt)_2]\cdot 2H_2O$	1×10^{-2}[b]			150
$Cu[Ni(mnt)_2]_2\cdot 2H_2O$	1×10^{-2}[b]			150
$Cu[Pt(mnt)_2]_2\cdot 2H_2O$	2×10^{-4}[b]			150
$[Ni(dmopd)_2][Ni(mnt)_2]$	3.8×10^{-4}[c]	330	+355	100
$[Ni(opd)_2][Ni(mnt)_2]$	1.2×10^{-6}[b]		+40	100
$[Ni(opd)_2]_2[Ni(mnt)_2]$	7.9×10^{-6}[b]		−700	100
$[Ni(dmopd)_2]_2[Ni(mnt)_2]$	1×10^{-7}[b]			100
$CV[Ni(mnt)_2]$	3.2×10^{-9}[b]			100
$An_3C[Ni(mnt)_2]$	3.2×10^{-9}[b]			100
$MG[Ni(mnt)_2]$	3.2×10^{-9}[b]			100
$NMP[Ni(mnt)_2]$	2×10^{-8}[b]			100
$Thian[Ni(mnt)_2]$	3.3×10^{-5}[b]			100
	10^{-4}[b]			154
$TMPD[Ni(mnt)_2]$	2.1×10^{-6}[c,d]		−500	100
	1.3×10^{-7}[c]			124
$TTF[Ni(mnt)_2]$	1.6×10^{-3}[c]	150	−655	100
$TTF[Pd(mnt)_2]$	2.1×10^{-4}[b]		−230	100
$TTF[Pt(mnt)_2]$	1.4×10^{-4}[b] $<10^{-6}$[b,f]		−410	100, 155
$(TTF)_2[Ni(mnt)_2]$	1.3×10^{-5}[b] $<10^{-6}$[b,f]		+30	100, 155
$(TTF)_2[Pt(mnt)_2]$	$<10^{-6}$[b,f]			155
$TCNTTF[Ni(mnt)_2]$	3.3×10^{-8}[b]			100

TABLE 5 (continued)

Compound[a]	Conductivity (Ω^{-1} cm^{-1})	ΔE (meV)	S (310 K) (μV deg^{-1})	References
TTT[Ni(mnt)$_2$]	3.1×10^{-3}[b]		−170	100
TTT[Pt(mnt)$_2$]	1×10^{-2}[b]			156
(TTT)$_2$[Pt(mnt)$_2$]	3×10^{-1}[b]			156
(TTT)$_2$[Pd(mnt)$_2$]	2×10^{-4}[b]			156
(perylene)$_2$[Ni(mnt)$_2$]	50[c]	102		101
(perylene)$_2$[Pd(mnt)$_2$]	7×10^{-2}[b]	168	+30	101, 119
(perylene)$_2$[Pt(mnt)$_2$]	300–400[c]		+28	119
(mb)$_2$[Ni(mnt)$_2$]	4.5×10^{-10} to 3×10^{-8}[b]			157
	1×10^{-9}[b]			102
(mb)$_2$[Pd(mnt)$_2$]	10^{-12} to 5×10^{-10}[b]			157
(mb)$_2$[Pt(mnt)$_2$]	7×10^{-10} to 2×10^{-9}[b]			157
mb[Ni(mnt)$_2$]	3×10^{-10} to 3×10^{-5}[b]			157
	6×10^{-7}[b]	207		102
mb[Pd(mnt)$_2$]	1×10^{-10} to 1×10^{-8}[b]			157
mb[Pt(mnt)$_2$]	5×10^{-10} to 2×10^{-6}[b]			157
	1×10^{-5}[c]	238		
(MV)$_2$[Ni(mnt)$_2$]	4×10^{-9}[b]			122
MV[Ni(mnt)$_2$]	2×10^{-9}[b]			122
BEDT-TTF[Ni(mnt)$_2$]	1×10^{-6}[c]	360		132
BEDT-TTF[Pd(mnt)$_2$]	2×10^{-4}[c]	197		132
BEDT-TTF[Pd(mnt)$_2$]$_2$	1.1×10^{-3}[c]	227		132
BEDT-TTF[Pt(mnt)$_2$]$_2$	1.5×10^{-6}[b]	327		132
[Au(TTP)][Ni(mnt)$_2$]	4×10^{-9}[b]	146		130
[Au(TTP)][Pt(mnt)$_2$]	1×10^{-9}[b]	180		130
[Cu(S$_2$CNR$_2$)$_2$][Ni(mnt)$_2$]	10^{-4}–10^{-5}[b,e]	240–330		158

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[a]Abbreviations: mb, methylene blue; MG, malachite green; MV, methyl viologen(1,1′-dimethyl-4,4′-bipyridinium cations); [Au(TPP)]$^+$, tetraphenylporphyrinato gold(III); BEDT-TTF, bisethylenedithiolatetetrathiafulvalene; TTT, tetrathiatetracene; TCNTTF, 4,4,5,5-tetracyano-$\Delta^{2,2}$-bis-1,3-dithiole tetracyanotetrathiafulvalene; TTF, tetrathiafulvalene; TMPD, (Wursters Blue) *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine; Thian, thianthrene; NMP, *N*-methylphenazinium; An$_3$C, tris(3-methoxyphenyl)carbene; CV, crystal violet; dmopd, 4,5-dimethyl-1,2-phenylenediimine; opd, 1,2-phenylenediimine. [b]Disc measurement. [c]Single crystal measurement. [d]The ESR of cobalt impurities in (TMPD)$_2$[Ni(mnt)$_2$] and (TMPD)$_2$[Pt(mnt)$_2$] has been examined. [e]The R substituents reported were Et, n-Pr and n-Bu. [f]The pellets were measured in ohms only.

nium]$[Ni(S_2C_2(CN)_2)_2]$[126], [*N*-methylphenazinium]$_2[Ni(S_2C_2(CN)_2)_2]$ [128] and [tropylium]$[Ni(S_2C_2(CN)_2)_2]$ [129] have been determined. The preparation and properties of the quasi one-dimensional complexes $[Au(TPP)][M(S_2C_2(CN)_2)_2]$ have also been described (where M = Ni, Pt and Au; TPP = tetraphenylporphyrinate ion) [130]. The crystal structure of the platinum complex has been determined and shows a mixed anion–cation one-dimensional stack with a distance of 3.70 Å in the stack [131]. A series of charge transfer complexes has been prepared by electrocrystallisation containing the organic donors BEDT-TTF and TMTSF and $[M(S_2C_2(CN)_2)_2]^{n-}$ (where M = Ni, Pd and Pt; $n = 1$ or 2) [132]. The crystal structure of BEDT-TTF$[Ni(S_2C_2(CN)_2)_2]$, a low temperature superconductor, has recently been resolved [15] (the super-conductivity of this compound has only been preliminarily reported).

The crystal structures have been resolved on a wide range of systems containing large countercations. These have not produced systems with significantly high conductivity [133–135].

ESR studies have also been carried out on $[TMPD]_2[Ni(S_2C_2(CN)_2)_2]$ [99]. However there is much more interest in ESR studies on impurity effects of copper(II) and cobalt(II) in single crystals of the nickel and platinum maleonitriledithiolate complexes. ESR studies have been carried out on $[TMPD]_2[Cu_xNi_{1-x}(S_2C_2(CN)_2)_2]$ [136] and $[TMPD]_2[Co_xM_{1-x}(S_2C_2(CN)_2)_2]$ (where M = Ni or Pt) [137], $[N(C_4H_9)_4]_2[Cu(S_2C_2(CN)_2)_2]$ diluted with nickel(II) complex [138] and $[N(C_4H_9)_4][Pd(S_2C_2(CN)_2)_2]$ diluted with the gold(III) complex [139].

Miller et al. [140] have very recently reported the preparation, crystal structure and magnetic susceptibility of the 1:1 decamethylferrocenium salts of the planar radical anion, bis(dithiolato)metalates: ($[Fe(C_5Me_5)_2]^{\cdot+}[M(S_2C_2(CN)_2)_2]^{\cdot-}$ (M = Ni and Pt) and $[Fe(C_5Me_5)_2]^{\cdot+}[Ni(S_2C_2(CF_3)_2)_2]^{\cdot-}$. The platinum maleonitriledithiolate complex was prepared in two different crystal structures. $[Fe(C_5Me_5)_2]^{\cdot+}[Ni(S_2C_2(CF_3)_2)_2]^{\cdot-}$ had a DADA stack structure in both axes and has the highest Weiss constant out of the four complexes. This complex has ferromagnetic coupling similar to that found for $[(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ [141].

The structure of the $[M(S_2C_2(CN)_2)_2]^{x-}$ (where M = Ni or Au; $x = 2$ and 1) and single crystals of $[(C_4H_9)_4N]_2[Ni_{1-x}Au_x(S_2C_2(CN)_2)_2]$ have been studied by X-ray emission and photoelectron spectroscopy [142,143]. Photoelectron spectroscopy has also been used to examine the platinum binding energies in the one-dimensional conductor α-LiPtmnt comparing them with those obtained for $[(C_2H_5)_4N][Pt(S_2C_2(CN)_2)_2]$ complexes [10b].

The magnetic susceptibility and redox properties of new complexes found between cluster cations with various dithiolene anions, 7,7,8,8-tetracyanoquinodimethane or tetracyanoethylene have been studied [144].

(iv) Linear polymers based on the bis-1,2-dithiolenes

There are a number of papers on linear polymers containing metal chelates of the 1,2-dithiolenes, in particular those based on tetrathiolate and tetrathiafulvalenetetrathiolate [145–147]. Manecke and Wöhrle [148] made an extensive study of the preparation and electrical conduction properties of the following complexes of the general formula $M'[M''(S_2C_2(CN)_2)_2]$ (where both Ms are first row transition metals). Recently a series of copper(II) complexes has been reported with the monoanionic and dianionic $[M(S_2C_2(CN)_2)_2]$ (where M = Ni, Pd and Pt). These were found to have the same conductivities, in the range 10^{-2}–10^{-6} Ω^{-1} cm^{-1} [149,150]. Furthermore a series of palladium and nickel tetrathiolene complexes has been studied by Reynolds et al. [151]. These were reported to have electrical conductivities in the range 20–0.23 Ω^{-1} cm^{-1}.

Studies on electropolymerised films of polypyrrole have also recently been carried out using $[Ni(S_2C_2(CN)_2)_2]^-$ and $[Pd(S_2C_2(CN)_2)_2]^-$ counter anions [152].

H. SOLID STATE PROPERTIES OF THE DIANION AND MONOANION BIS(MALEONITRILEDITHIOLATE) COMPLEXES

The solid state properties of a range of bis(1,2-dicyanoethylenedithiolato)-metalate complexes are known and these have been tabulated in Tables 3–5.

I. A DISCUSSION OF THE STRUCTURAL AND ELECTRONIC PROPERTIES OF THE $[M(S_2C_2(CN)_2)_2]^-$ COMPLEXES (M = Ni, Pd and Pt) WITH SMALL COUNTERCATIONS

Only the charge transfer complexes with perylene and TTF have high electrical conductivities. The $[M(S_2C_2(CN)_2)_2]^{x-}$ (where M = Ni, Pd and Pt; $x = 1$) complexes with small countercations form conducting systems in which the cation plays no part in the conduction process. The following is a discussion of the structural interactions and electronic factors that allow these properties to occur.

(i) The dithiolene dianion salts

The dithiolene dianions possess a completely filled HOMO and therefore there are no possibilities of any anion–anion interactions in the solid state; this is known as a Mott–Hubbard semiconductor. The structures of the dianion salts therefore consist of non-interacting anions packed in the most efficient way, depending on the relative sizes of the anions and cations. The structures reported to date in the literature have only contained large countercations. The crystal structure of $Rb_2[Ni(S_2C_2(CN)_2)_2]\cdot H_2O$ has been examined and reveals that the anions are closer than with the larger countercations. The reflectance spectra of the $[M(S_2C_2(CN)_2)_2]^{2-}$ (where M = Ni, Pd and Pt) complexes have all been found to have high absorbances in the visible region which indicates some solid state interactions [73,74].

(ii) The dithiolene monoanion salts

The dithiolene monoanions each contain one electron in the HOMO and therefore enable the anions to interact with one another in a number of ways. However, at low temperatures, the interactions between anions may be greater than $4t$ (transfer integral) and this can give rise to a number of possible structural/electronic interactions.

(a) If the equidistant stacked structure is maintained and overlap of the HOMO occurs, this can result in two possible ground states. In the first state the electrons would be delocalised throughout the stack. This would correspond to the situation where the overlap integrals were much greater than the value of the electron–electron Coulomb repulsion energy U. The stack would then exhibit metallic properties including high electrical conductivity. However, since there is one electron per molecule, the conduction band would be exactly half filled. The Peierls instability for the half-filled band case is extremely strong and it would be expected that the equidistant stack would be unstable with respect to a lattice distortion. This produces a bandgap of the Fermi surface and consequently semiconducting properties. Within the dimer pair, the extent of overlap of the HOMOs could be relatively weak which could result in magnetic properties in which the singlet ground state and thermally accessible triplet state were present.

(b) If, however, U is much greater than $4t$, electrons will be localised on the individual anions within the equidistant stack. Such a system will be a semiconductor but will have the magnetic properties of a Heisenberg antiferromagnetic chain.

These two possibilities appear to be exemplified in the monoanion dithiolene salts of small cations. In the nickel series of compounds where the $3d$ orbitals of the nickel are relatively small, U appears to be considerably greater than $4t$ and an equidistant stacked structure is preserved which is semiconducting and has the magnetic properties of the Heisenberg antiferromagnetic chain. At low temperature there appears to be a transition which results in dimer formation and a singlet ground state. The cause of this transition is not known at present. On the other hand the platinum series of compounds appear to represent the case where the overlap integral is much greater than U. These compounds have dimer pairs of anions within a stack structure resulting in semiconducting properties. This could be accounted for by the presence of the much larger platinum $5d$ orbitals which enhance interactions between the molecules and hence stabilise the Peierls distorted state.

However, a third possibility exists when the compounds are prepared by oxidation of the dianion. Oxidation of the materials may not necessarily result in the production of an integral oxidation state compound. These form equidistant stacked structures in which the electrons are delocalised to form a band. There may be a degree of band filling in which the system is of a lower energy state than that corresponding to the half-filled band case. Such systems are well known for the tetracyanoplatinates and the bis(oxalato)platinates. Indeed the platinum bis(dithiolene) α-LiPtmnt complex has been well characterised and possesses an equidistant stack structure with a band filling of 0.59.

It is clear from the studies undertaken to date that the size of the countercation plays an important role in determining the ground state properties of the resulting material. The one-dimensional metallic state appears to be favoured by the presence of very small countercations such as lithium or magnesium. Similarly, equidistant stack structures in the nickel series of compounds are favoured by the smaller Group I cations. The caesium salt, however, appears to have a dimeric structure and to have a partially filled band less than the half-filled band case for a single monoanion and therefore less than the quarter-filled band for the dimer of anions. The palladium series of compounds represents the most complicated case. In the caesium salt the stack structure is not maintained and the palladium monoanions exist as dimer pairs in a complicated packing arrangement which gives rise to short sulphur–sulphur contacts in two orthogonal directions. It is these unusual two-dimensional interactions of the dianions which give rise to the high conductivity and metallic properties of this compound when subjected to high pressures [12,90].

J. GENERAL CONCLUSIONS AND OUTLOOK TOWARDS OTHER RELATED SYSTEMS

The incorporation of small counter cations with $[M(S_2C_2(CN)_2]^{x-}$ (where $M = Ni$, Pd or Pt; $x = 1$ or non-integral) anions produces a variety of stacked structures. The nature of the stacking is dependent on central metal, oxidation state, tilt of the anion, degree of S–S interactions and the size of the counter cations. In terms of the electronic requirement, single electrons on each of the anions can either repel each other due to a large U (coulomb–coulomb repulsion) or attract each other due to a large $4t$ (transfer integral). A non-integral oxidation state produces metallic properties due to incomplete band-filling.

The charge transfer complexes with the $[M(S_2C_2(CN)_2)_2]^{x-}$ ($M = Ni$, Pd or Pt; $x = 1$ or 2) acceptors all have low conductivities; exceptions are however found with perylene and tetrathiatetracene donors.

The optical properties of the bis(1,2-dithiolenes) is the other main area of research on these compounds. The photooxidation process in the bis(1,2-dithiolenes) has given rise to a variety of technological applications.

The effect of changing the ligand to 4,5-dimercapto-1,3-dithiole-2-thione (dmit) $(C_3S_5)^{2-}$ produces an extended ring containing more sulphur.

A number of workers have been involved in the preparation of the charge transfer complexes of $[M(S_3C_5)_2]^{x-}$ (where M = Ni, Pd and Pt; $x = 1$ and 2). Also a series of partially oxidised complexes has been reported (see refs. 13, 14, 159–165 for examples). Salts with small countercations such as the alkali metals, have also been prepared and studied. These generally have higher conductivities than the bis(maleonitriledithiolate) complexes [166–169]. The extended ring system has a greater degree of two-dimensional interactions than the bis(maleonitriledithiolate) complexes due to the increased overlap of adjacent sulphur atoms in and between stacks of anions [170]. The caesium salts of $[Pd(S_3C_5)_2]^-$ and $[Pd(S_2C_2(CN)_2)_2]^-$ have been compared in a recent paper [171]. Groups working on organic charge transfer solids are currently investigating unsymmetrical donors and acceptors, different ligands readily attached to the central metal. Interesting systems have also been produced by changing to NH, Se and Te rather than S. All these possibilities are available with the inorganic based anions. Further investigation is required in order to give a better understanding of the structural/electronic properties of these materials.

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