

# Derivatives of Magnus' Green Salt

FROM INTRACTABLE MATERIALS TO SOLUTION-PROCESSED TRANSISTORS

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*Magnus' green salt is a quasi-one-dimensional compound of composition  $[Pt(NH_3)_4][PtCl_4]$  comprising linear arrays of platinum(II) ions. It is essentially insoluble in water and organic solvents and therefore difficult to process, which limits its use. Recently, soluble and thus processible derivatives of Magnus' green salt have been synthesised by substituting the ammonia by linear and branched aminoalkanes. The Pt-Pt distances and the properties of these Magnus' salt derivatives depend on the detailed structure of the aminoalkane. In particular, in compounds with branched aminoalkanes weak but noteworthy interactions arise between adjacent platinum atoms, as is evident from their colour, their electrical conductivity, and their UV and IR spectra. Compounds with optically active branched aminoalkanes exhibit circular dichroism with a bisignate Cotton effect and unusually high absolute values for the chiral anisotropy factors. The complex  $[Pt(NH_2dmoc)_4][PtCl_4]$  with dmoc designating (S)-3,7-dimethyloctyl is of particular importance since its colour and electrical conductivity strongly resemble those of Magnus' green salt. Films of  $[Pt(NH_2dmoc)_4][PtCl_4]$  can function as an active semiconducting layer in field effect transistors. Remarkably, such devices have superior stability in air and water to unprotected field effect transistors fabricated with typical organic polymers. Hence, Magnus' salt derivatives might find use in components of mass-produced "plastic electronics".*

Magnus' green salt,  $[Pt(NH_3)_4][PtCl_4]$ , was first prepared by Gustav Magnus around 1830 by the dissolution of platinum(II) chloride in hydrochloric acid followed by addition of ammonia (1, 2). The green crystals which slowly precipitated attracted considerable attention as characterised ammonia complexes were rare at that time. Since then several procedures for synthesising Magnus' green salt have been developed, for example, with the starting materials  $PtCl_2$  and ammonia (3–5);  $K_2[PtCl_4]$  and ammonia (6, 7, 8);  $PtCl_2$  and  $[Pt(NH_3)_4]Cl_2$  (9);  $K_2[PtCl_4]$  and  $[Pt(NH_3)_4]Cl_2$  (10–13); or  $(NH_3)_2[PtCl_4]$  and  $[Pt(NH_3)_4]Cl_2$  (14).

Although the elemental composition of Magnus' green salt was correctly analysed by Magnus himself (1, 2), a detailed insight into the structure of Magnus' green salt developed only slowly over a very long period. Initially, confusion arose due to the early discovery of *cis*- $[Pt(NH_3)_2Cl_2]$  (Peyrone's chloride (9, 15)) and *trans*- $[Pt(NH_3)_2Cl_2]$  (Reiset's second chloride (5, 16–18)) which possess the same stoichiometric composition as Magnus' green salt. While some authors attributed Magnus'

green salt to a stoichiometric mixture of  $[Pt(NH_3)_4]Cl_2$  and  $PtCl_2$  (9, 15), other authors, around the year 1850, tried to explain the nature of platinum(II)-ammonia complexes on the basis of a condensed state of two ammonia molecules ( $N_2H_6$ ) and two modifications of atomic platinum states (19–23). One form of the platinum states was called 'platinicum', and given the symbol pt. Platinicum, was believed to occur only as dimers ( $pt_2$ ). The other form was regarded as a condensed state of  $pt_2$  and was designed as 'platinosum' and connected with the symbol Pt.

It was suggested that hydrogen atoms in ammonia or in the condensed state of ammonia could be substituted by the respective equivalents of 'platinicum' or 'platinosum', resulting in moieties such as  $NH_2Pt$  (platosamine),  $N_2H_5Pt$  (diplatosamine),  $NHpt_2$  (platinamine), and  $N_2H_4pt_2$  (diplatinamine).

In 1886, it was realised that the proposed conversions of N-H into N-Pt bonds could not describe the nature of platinum-ammonia complexes because pyridine does not contain N-H bonds but nonetheless forms complexes analogous to those

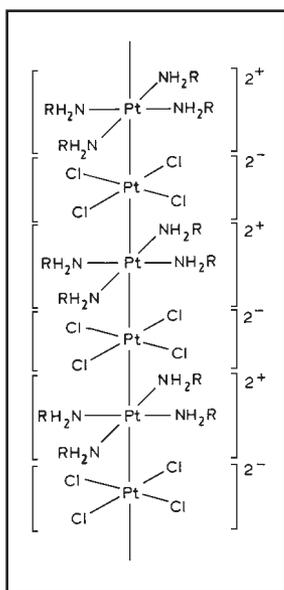


Fig. 1 Schematic representation of the quasi-one-dimensional structure of compounds of composition  $[Pt(NH_2R)_4][PtCl_4]$   $R = H$  (Magnus' green salt) or  $R = \text{alkyl group}$

of ammonia, for example,  $[Pt(\text{pyridine})_2Cl_2]$  and  $[Pt(\text{pyridine})_4][PtCl_4]$  (24). As an alternative, the isomers were interpreted with the help of pentavalent nitrogen atoms, which allow the formation of, for instance,  $Pt(-NH_3-Cl)_2$  or  $Cl-Pt-NH_3-NH_3-Cl$  entities (24). By 1906 it was known from experiments that Magnus' green salt was composed of  $PtCl_4$  and  $Pt(NH_3)_4$  moieties, but the structure of Magnus' green salt was still explained using pentavalent nitrogen atoms. This resulted in the following possibilities (25):  $Pt(-Cl-Cl-NH_3-NH_3-Pt-NH_3-NH_3-Cl-Cl)_2Pt$  and  $Pt(-NH_3-NH_3-Cl-Cl)_2Pt$ .

It is noteworthy that as late as 1930 discussions about the general structure of platinum complexes had not ended (26); indeed, the detailed structure of Magnus' green salt was finally elucidated only in 1957 by X-ray diffraction, revealing alternately stacked  $[Pt(NH_3)_4]^{2+}$  and  $[PtCl_4]^{2-}$  moieties comprising linear arrays of platinum atoms separated by 3.25 Å, see Figure 1 (27). This distance is significantly larger than the typical Pt-Pt bond lengths of 2.6–2.8 Å (28–35). Hence, it was suggested that it was mainly the electrostatic interactions between the oppositely charged coordination units that lead to the stacking of the coordination units of Magnus' green salt into a quasi-one-dimensional structure, rather than bonds between the platinum atoms (36, 37). Nonetheless, Pt-Pt interactions

involving the  $6p_z$  atomic orbitals, although weak, also exist (36) and, in fact, are the origin of important materials' properties – as will become evident.

### Magnus' Pink Salt

A pink or red isomer of Magnus' green salt, usually designated as Magnus' pink salt, has also been described. Some authors (38, 39) attributed the first synthesis of Magnus' pink salt to Vauquelin in 1817 (40, 41), but we failed to find evidence for such a compound in the related reports (it appears that the corresponding red substances concern platinum(IV) complexes). In 1906, the discovery of Magnus' pink salt was ascribed to a student named Bjerrum, and it was deduced that Magnus' pink salt had the composition  $[Pt(NH_3)_4][PtCl_4]$  (25). Remarkably, the detailed structure of Magnus' pink salt is still unknown, since attempts to get crystals suited for single-crystal X-ray diffraction have failed (27, 42). It could be concluded from powder X-ray diffraction patterns, however, that the platinum atoms in Magnus' pink salt are separated by more than 5 Å (27). The formation of Magnus' pink salt seems to be kinetically favoured, but it readily converts to Magnus' green salt during synthesis if it is not prepared at low temperatures and rapidly dried (43). Once isolated, however, it can be stored for months or years under ambient atmosphere.

### Derivatives of Magnus' Green Salt

Motivated by the existence of Magnus' green salt, numerous compounds of the type  $[PtL_4]^{2+}[PtL'_4]^{2-}$  (L and L' are ligands or coordinating parts of multidentate ligands) have been produced, and an overview has been presented in the literature (44). Indeed, complexes with structures investigated by X-ray analysis reveal a linear backbone of platinum atoms separated by distances of 3.1–4.0 Å, depending on the ligands (44, 45). A systematic dependence of the interplatinum distance on the nature of the ligands has not yet been found and, remarkably, compounds with two different Pt-Pt spacings also exist (44).

This paper will focus on compounds of the type  $[Pt(NH_2R)_4][PtCl_4]$  with R denoting an alkyl group, see Figure 1. Such complexes have been typically

prepared in aqueous solution from  $K_2[PtCl_4]$  and  $[Pt(NH_2R)_4]Cl_2$  (46);  $K_2[PtCl_4]$  and the 1-aminoalkane (7, 24, 43); or  $PtCl_2$  and the 1-aminoalkane (47).

### Derivatives with Linear 1-Aminoalkanes

Of the compounds with linear 1-aminoalkanes reported so far, only the aminomethane complex has been noted to be green (25, 37, 46–50). Its Pt-Pt spacings (3.25–3.29 Å (7, 49, 51)) are similar to those of Magnus' green salt (see above). Compounds with linear 1-aminoalkanes ranging from aminoethane to 1-aminotetradecane are, however, pink (or reddish) (37, 43, 46, 49). For R = ethyl, butyl, propyl and 2-methylpropyl (47, 50, 52), brown or greenish-grey modifications were also described but there is evidence that these products were not (pure) Magnus' salt derivatives (43). However, single crystals of any of the pink compounds suitable for X-ray analysis have so far only been obtained for the aminoethane derivative, revealing linearly arranged platinum atoms separated by 3.62 Å (49), well below the Pt-Pt distance in Magnus' pink salt (see above). Remarkably, the plane of the platinum-nitrogen coordination square of the tetrakis(aminoethane)platinum(II) coordination unit is inclined by 29° to that of the tetrachloroplatinate(II) plane (49), indicating that not only electrostatic attractions, but also crystal packing effects determine the Pt-Pt distance.

### Derivatives with Branched 1-Aminoalkanes

Interestingly, the colours of the Magnus' salt derivatives with branched 1-aminoalkanes prepared so far (45, 53) differ from the colour of related complexes with linear 1-aminoalkanes of similar chain lengths, although it was claimed earlier (46) that aminoalkanes with two or more carbon atoms only give rise to pink Magnus' salt derivatives due to an increase in the Pt-Pt distance by the packing of the alkyl groups. The complex  $[Pt(NH_2dmoc)_4][PtCl_4]$  (dmoc is (*S*)-3,7-dimethyloctyl) is crystalline, exhibits the colour of Magnus' green salt and is characterised by a Pt-Pt distance of 3.1 Å. The 1-amino-2-ethylhexyl ( $NH_2$  eh) (eh is ethylhexyl) Magnus' salt derivative is dark violet (or greyish: probably depending on the surface roughness of the solids or differences in

light reflection), apparently similar in colour to  $[Pt(en)_2][PtCl_4]$  (en = 1,2-diaminoethane) (51) which exhibits an interplatinum distance of 3.41 Å (7). Since the colour of  $[Pt(NH_2R)_4][PtCl_4]$  complexes appears to be related to the interplatinum spacings, the Pt-Pt distance in  $[Pt(NH_2eh)_4][PtCl_4]$  is probably smaller than that of the pink compounds but similar to that in  $[Pt(en)_2][PtCl_4]$ . However, upon cooling,  $[Pt(NH_2eh)_4][PtCl_4]$  undergoes a reversible colour change to green at ca. -55°C, which is probably connected with a diminishing Pt-Pt distance (the pink derivatives with linear 1-aminoalkanes stay pink to at least -196°C). Differential scanning calorimetric (DSC) measurements did not reveal a pronounced energy change in the temperature region of the colour change at -55°C. Besides the colour transition,  $[Pt(NH_2eh)_4][PtCl_4]$  differs from the other 1-aminoalkane derivatives by its essentially amorphous state – evident from polarisation microscopy and X-ray diffraction.

### Colour, IR and UV-Vis Spectra

As already evident from the above section, the colour of  $[Pt(NH_2R)_4][PtCl_4]$  complexes depends on the substituent. In the case of methyl and (*S*)-3,7-dimethyloctyl groups it is green; for complexes with linear alkyl groups comprising more than one carbon atom it is pink, and it is dark violet when R is 2-ethylhexyl. Indeed, it appears that the green colour is restricted to compounds with relatively short Pt-Pt distances; this is also reflected in the UV and IR spectra.

The Pt-Cl stretching vibration of the pink compounds emerges around 320  $cm^{-1}$ , which is close to the related frequency of  $K_2[PtCl_4]$ , but significantly different from those of Magnus' green salt (311  $cm^{-1}$ ),  $[Pt(NH_2eh)_4][PtCl_4]$  (306  $cm^{-1}$ ) and  $[Pt(NH_2dmoc)_4][PtCl_4]$  (303  $cm^{-1}$ ). The low absorption frequencies of the latter three compounds appear to indicate proximity between adjacent coordination units (10, 54). The UV-vis spectra of Magnus' green salt and its derivatives with significant Pt-Pt interactions, are of complex nature and have been discussed extensively in the literature (7, 8, 37, 46, 51, 55). The UV-vis spectra of Magnus' green salt and its alkyl derivatives mentioned above are dominated in the wavelength

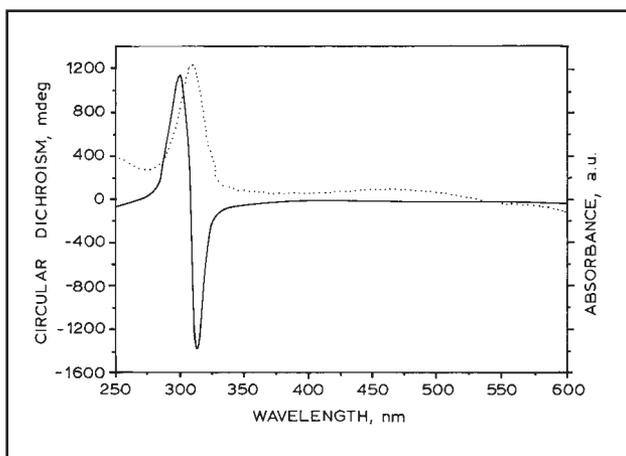


Fig. 2 Circular dichroism (CD) shown by the solid line, and the UV spectrum shown by the dotted line, for  $[\text{Pt}(\text{NH}_2\text{dmoc})_4][\text{PtCl}_4]$

range of 200–800 nm by a band in the UV region. Smaller peaks in the visible wavelength range appear to be due to  $d-d$  transitions, which may shift towards lower energies in compounds of the Magnus' salt type with metal-metal spacings in the region of 3.25–3.6 Å (7). Magnus' green salt and its aminomethane derivative (55) show an absorption maximum ( $\lambda_{\text{max}}$ ) at 290 nm in the solid state; solid  $[\text{Pt}(\text{NH}_2\text{dmoc})_4][\text{PtCl}_4]$  at 310 nm;  $[\text{Pt}(\text{NH}_2\text{eh})_4][\text{PtCl}_4]$  in the solid state at 292 nm and in tetrahydrofuran at 263 nm with a shoulder at  $\sim 290$  nm; and the solid aminoethane (55) and the 1-amino-octane derivative in tetrahydrofuran at 251 and 255 nm, respectively.

Thus, it seems that a band at  $\sim 300$  nm arises in the modifications that are not pink and is indicative of significant interactions between adjacent platinum atoms. The related band has been attributed to a transition of the  $d_{z^2}$  orbital of the  $[\text{PtCl}_4]^{2-}$  to the  $p_z$  orbital of the  $[\text{Pt}(\text{NH}_2\text{R})_4]^{2+}$  unit (7, 54). It should be noted that the UV spectra of the pink complexes are not simply composed of a superposition of the spectra of the respective cationic and anionic coordination units. This indicates that very weak Pt-Pt interactions are also present in the related pink complexes in spite of the presumably relatively large interplatinum distance in them.

### Circular Dichroism

The  $5d_{z^2}-6p_z$  charge transfer transition in Magnus' salt derivatives can be involved in circular dichroism (CD) induced by coordinated optically

active aminoalkanes (56). Generally, induction of CD can proceed via association of optically active molecules in the second coordination sphere (outer-sphere association, for example, via dispersion interactions (57, 59)), where the optically active moieties do not show a preferential orientation with respect to the coordination sphere (59). Induced CD emerges in Magnus' salt derivatives of type  $[\text{Pt}(\text{NH}_2\text{R})_4][\text{PtCl}_4]$  where R denotes (*S*)-3,7-dimethyloctyl or (*R*)-2-ethylhexyl via hydrogen bonds (57, 58) or via dispersion interactions, respectively, (56). In the region of the  $5d_{z^2}-6p_z$  transition, the CD spectra of solid  $[\text{Pt}(\text{NH}_2\text{dmoc})_4][\text{PtCl}_4]$  and  $[\text{Pt}(\text{NH}_2\text{eh})_4][\text{PtCl}_4]$  reveal strong signals (see Figure 2 for example which also includes the related UV spectrum).

Surprisingly, a bisignate Cotton effect arises for both of the compounds, with a negative sign at lower energy (first Cotton effect at 314 nm or 291 nm, respectively) and a positive sign at higher energy (second Cotton effect at 298 nm or 276 nm, respectively), indicating strong exciton coupling between the chromophores. The negative sign of the first Cotton effect and the positive sign of the second Cotton effect imply a left-handed screwiness of the electric transition dipole moments of the neighbouring chromophores (negative exciton chirality) in both complexes. In general, in organic structures, the screwiness is commonly associated with a helical arrangement of the chromophores. Since the electric  $5d_{z^2}-6p_z$  transition is  $\pi$ -polarised (7, 55), the bisignate Cotton effect would – in

those terms – imply a left-handed helical arrangement of the platinum backbone. However, CD spectra of metal complexes should be regarded as a consequence of the chirality of the metal-ligand system as a whole, rather than of the individual chromophores (60). Hence, the helical feature in the Magnus' salt derivatives is not necessarily present in the platinum backbone itself.

The chiral anisotropy factors,  $g_{\text{abs}}$ , for both the  $\text{NH}_2\text{dmoc}$  and the  $\text{NH}_2\text{eh}$  derivatives are 0.10–0.12, and are larger than typical values reported for other transition metal complexes, including those found for induced CD in  $d-d$  transitions in Magnus' salt derivatives (59, 61) (the  $5d_{2z}-6p_z$  transitions were not mentioned in 59 and 61). Rather high chiral anisotropy factors – up to 0.06 – have been observed for cobalt(III) complexes with bidentate cyclohexane derivatives (62, 63) and for  $[\text{Pt}(\text{NH}_3)_2(\text{dmbn})]$  with  $\text{dmbn} = (\Delta)$ -3,3-dimethyl-1,2-butanediamine (64); but these values fall below those of  $[\text{Pt}(\text{NH}_2\text{dmoc})_4][\text{PtCl}_4]$ .

## Solubility and Processibility

Besides the chemical and structural aspects of Magnus' salts attention has also been paid to their material properties, for instance:

- the dichroism observed with linearly polarised light of Magnus' green salt (7–10, 37, 55) and its aminomethane (24, 46), aminoethane (46) and 1-aminobutane (24) derivatives, or
- the electrical semiconductivity (65–73) of Magnus' green salt, which appears to arise as a consequence of the above mentioned Pt-Pt interactions (electrical conductivity is higher in the direction of the platinum arrays than perpendicular to them, see also below), or
- the thermal and chemical stability, which had already been recognised by 1847, when it was described that Magnus' green salt is notably stable towards heat, acid and alkaline solutions (74), although it is decomposed at elevated temperatures by nitric acid (3).

Hence, Magnus' green salt and its derivatives are of interest to materials scientists, all the more so as their structures, see Figure 1, resemble those of rigid-rod polymers with a metal element main chain; this is a class of polymers which has

received relatively little attention. However, most Magnus' salt type complexes (including Magnus' green salt) are largely insoluble in water and organic solvents. This unfavourable property is typical of rigid-rod polymers and often severely restricts or even prevents potential applications. Only recently have soluble and therefore processible Magnus' salts been disclosed, in particular derivatives with linear 1-aminoalkanes in the range of heptyl to tetradecyl (the butyl-substituted compound is still insoluble in organic solvents and water), and the branched aminoalkanes mentioned above (43, 45, 53).

It was shown that the  $[\text{Pt}(\text{NH}_2\text{eh})_4]^{2+}$  and the  $[\text{PtCl}_4]^{2-}$  units assemble into supramolecular structures not only in the solid state but also in toluene, in the studied concentration range of 0.1–1.0% w/w and temperature 37°C, as evident from investigations with membrane osmometry. The measurements yielded a number average molecular weight ( $M_n$ ) of  $4 \times 10^5 \text{ g mol}^{-1}$ , which corresponds to a supramolecular assembly containing ca. 750 platinum atoms. The existence of high molecular weight structures composed of  $[\text{Pt}(\text{NH}_2\text{eh})_4]^{2+}$  and  $[\text{PtCl}_4]^{2-}$  in toluene at 37°C was qualitatively confirmed by viscosimetric measurements and its extremely sluggish dissolution behaviour (a property characteristic of high molecular weight substances).

The  $M_n$  of  $[\text{Pt}(\text{NH}_2\text{dmoc})_4][\text{PtCl}_4]$ , determined by vapour phase osmometry in toluene in the concentration range 0.1–1.15% w/w at 70°C, resulted in a value of  $9 \times 10^3 \text{ g mol}^{-1}$ , which corresponds to about 16 platinum atoms in an assembled formation. The existence of supramolecular structures in solution implies that electrostatic attraction between the oppositely charged coordination units indeed plays an important role in the formation of the quasi-one-dimensional structures of Magnus' salts.

The complexes with long linear 1-aminoalkanes dissolved preferentially at elevated temperature. Hot solutions of these complexes converted, upon cooling to room temperature, into pink gels above a concentration of ca. 0.1–0.5% w/w. These gels are stable for months. The gelation process is thermally reversible and, hence, appears to be associated with an ordering or crystallisation

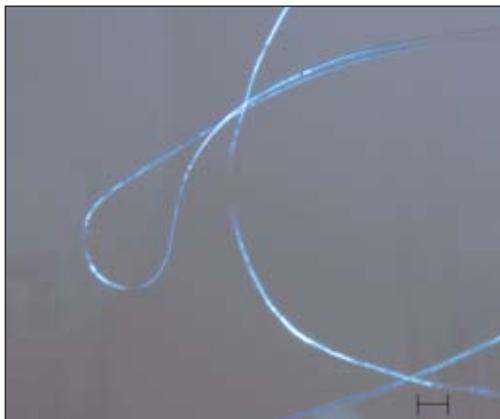


Fig. 3 Polarised optical microscope image of a fibre of  $[Pt(NH_2R)_4][PtCl_4]$ ,  $R = 2\text{-ethylhexyl}$ ; prepared by electrostatic spinning. The Pt complexes were oriented in the fibres  
Scale 100  $\mu m$

process. When observed in the optical microscope, the gels reveal birefringent, highly ordered, fibrillar structures. The birefringence is lost when the gels are heated to adopt the fluid state again. TEMs of dried gels show fibrillar structures of typical width between 20 nm and 3  $\mu m$ , and are indicative of a collapsed network. Importantly, the dried gels can again be dissolved at elevated temperatures, and the resulting solutions again form gels upon cooling to room temperature. In contrast to the Magnus' salt derivatives with linear 1-aminoalkanes, solutions of  $[Pt(NH_2eh)_4][PtCl_4]$  did not yield gels when cooled from elevated temperature to room temperature, while  $[Pt(NH_2dmoc)_4][PtCl_4]$  in the concentration range of 2–5% w/w in toluene separated into a solvent and a thermo-reversible gel-like phase upon cooling from 80°C to room temperature.

### Fibres, Films and Electronic Devices

Due to their outstanding solubility/processibility, fibres and films have been readily obtained for compounds of type  $[Pt(NH_2R)_4][PtCl_4]$  where R is 1-amino-octane, 1-amino-2-ethylhexane and (*S*)-1-amino-3,7-dimethyloctane (43, 75, 76). Fibres, see Figure 3, were manufactured by electrostatic spinning. Polarisation microscopy disclosed that the platinum complexes were oriented in the fibres as well as in film. Films comprising oriented structures of the 1-amino-octane derivative could be

prepared by manual stretching of related gels (see above). The growth of highly oriented films of  $[Pt(NH_2dmoc)_4][PtCl_4]$  and  $[Pt(NH_2eh)_4][PtCl_4]$  proceeded well by deposition of the compounds from super-saturated solutions onto glass slides covered by a thin layer of highly oriented poly-(tetrafluoroethylene) (PTFE) that had been friction deposited onto the slides at elevated temperature (77). Parallel strips of very long, needle-like  $[Pt(NH_2dmoc)_4][PtCl_4]$  crystals, which were oriented along the PTFE molecules, were readily detected in the films in TEM images.

Outstanding orientation in the arrays of the coordination planes in the  $[Pt(NH_2dmoc)_4][PtCl_4]$  units was evident from atomic force microscopy (AFM), see Figure 4, and also from electron diffraction patterns. The orientation of  $[Pt(NH_2dmoc)_4][PtCl_4]$  in the films was also evident from the UV-vis absorption spectra recorded with polarised light with the incident light polarised parallel and perpendicular to the platinum arrays. In the parallel case, the absorption maximum at 310 nm was substantially more pronounced than at perpendicular orientation. An analogous phenomenon was observed in the UV-vis absorption spectra of



Fig. 4 Atomic force microscopy (AFM) image of an oriented  $[Pt(NH_2dmoc)_4][PtCl_4]$  film showing parallel stripes, each built up of linearly assembled coordination units  
Image size  $\sim 18 \times 20$  nm

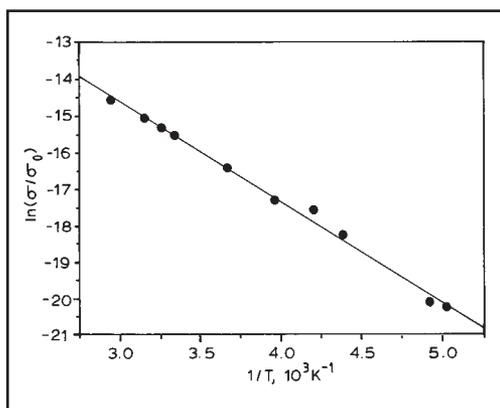


Fig. 5 Dependence of the logarithm of the conductivity ( $\sigma$ ) of a pressed sample of  $[\text{Pt}(\text{NH}_2\text{dmoc})_4][\text{PtCl}_4]$  on the inverse temperature ( $1/T$ ), with  $\sigma_0 = 1 \text{ S cm}^{-1}$

oriented  $[\text{Pt}(\text{NH}_2\text{ch})_4][\text{PtCl}_4]$  films.

The bulk electrical conductivity of pressed samples of  $[\text{Pt}(\text{NH}_2\text{dmoc})_4][\text{PtCl}_4]$  was  $1.6 \times 10^{-7} \text{ S cm}^{-1}$  at room temperature, which is in the range of that found for pressed samples of Magnus' green salt measured under similar conditions ( $5 \times 10^{-6} \text{ S cm}^{-1}$ ). The pressed samples typically are pellets of ca. 1 cm diameter that are pressed under a load of a few tons. In oriented films, the conductivity parallel to the platinum arrays ( $10^{-4}$  to  $10^{-3} \text{ S cm}^{-1}$ ) was several orders of magnitude higher than the values for the perpendicular orientation (ca.  $10^{-8} \text{ S cm}^{-1}$ ). These anisotropic conductivities are consistent with a mobile charge path via the platinum

arrays. The temperature dependence of the conductivity of pressed samples followed the expression:

$$\sigma = \sigma_0 e^{\frac{E_a}{k_B T}}$$

where  $\sigma$  is electrical conductivity,  $\sigma_0$  is an arbitrary constant,  $E_a$  is the activation energy,  $k_B$  is Boltzmann's constant, and  $T$  the temperature (in K). This temperature dependence is characteristic for semiconductors with a single thermally activated conduction process in the observed temperature interval (70), and, in agreement with the above equation, a logarithmic representation of the conductivity versus the inverse temperature resulted in a straight line, see Figure 5. From its slope an activation energy of 0.24 eV was calculated, which is in the range of the values reported for Magnus' green salt (0.1–0.4 eV) (67–70). Hence,  $[\text{Pt}(\text{NH}_2\text{dmoc})_4][\text{PtCl}_4]$  may indeed be regarded as a soluble equivalent of Magnus' green salt.

The intrinsic mobility of charge carriers in  $[\text{Pt}(\text{NH}_2\text{dmoc})_4][\text{PtCl}_4]$  was determined with the pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) technique, resulting in a mobility along the Pt-chains of  $0.06 \text{ cm}^2 \text{ Vs}^{-1}$  (76). This value compares favourably with those found for  $\pi$ -stacked discotic materials and  $\pi$ -bond conjugated polymers (78, 79). One should be aware that the PR-TRMC technique yields mobilities of the trap-free state, that is, mobilities expected to be

#### Selected Data for Magnus' Salts and Magnus Salt Derivatives of Type $[\text{Pt}(\text{NH}_2\text{R})_4][\text{PtCl}_4]$

$d(\text{Pt-Pt})$  denotes the interplatinum distance;  $\sigma$  the electrical conductivity at room temperature;  $\lambda_{\text{max}}$  the absorption maximum wavelength in the UV-vis region; and  $\nu(\text{Pt-Cl})$  the position of the IR absorption of the Pt-Cl stretching vibration

| Compound              | Colour                | $d(\text{Pt-Pt})$ ,<br>$\text{\AA}$ | $\sigma$ ,<br>$\text{S cm}^{-1}$ | $\lambda_{\text{max}}$ ,<br>$\text{nm}$ | $\nu(\text{Pt-Cl})$ ,<br>$\text{cm}^{-1}$ |
|-----------------------|-----------------------|-------------------------------------|----------------------------------|---|---|
| Magnus' green salt    | green                 | 3.24 <sup>(b)</sup>                 | $5 \cdot 10^{-6}$                | 290                                     | 311                                       |
| Magnus' pink salt     | pink                  | > 5                                 | n.a.                             | n.a.                                    | 321                                       |
| R = methyl            | green                 | 3.27 <sup>(c)</sup>                 | n.a.                             | 290                                     | n.a.                                      |
| R = ethyl             | pink                  | 3.62                                | n.a.                             | 251                                     | n.a.                                      |
| R = octyl             | pink                  | n.a.                                | $< 10^{-10}$                     | n.a.                                    | 319                                       |
| R = 2-ethylhexyl      | violet <sup>(a)</sup> | n.a.                                | $7 \cdot 10^{-10}$               | 292                                     | 306                                       |
| R = 3,7-dimethyloctyl | green                 | 3.1                                 | $2 \cdot 10^{-7}$                | 310                                     | 303                                       |

(a) or greyish, depending on the observation angle; at ca.  $-55^\circ\text{C}$  reversible colour transition to green

(b) reported values ranging from 3.23–3.25  $\text{\AA}$  (c) reported values ranging from 3.25–3.29  $\text{\AA}$  n.a. = not applicable

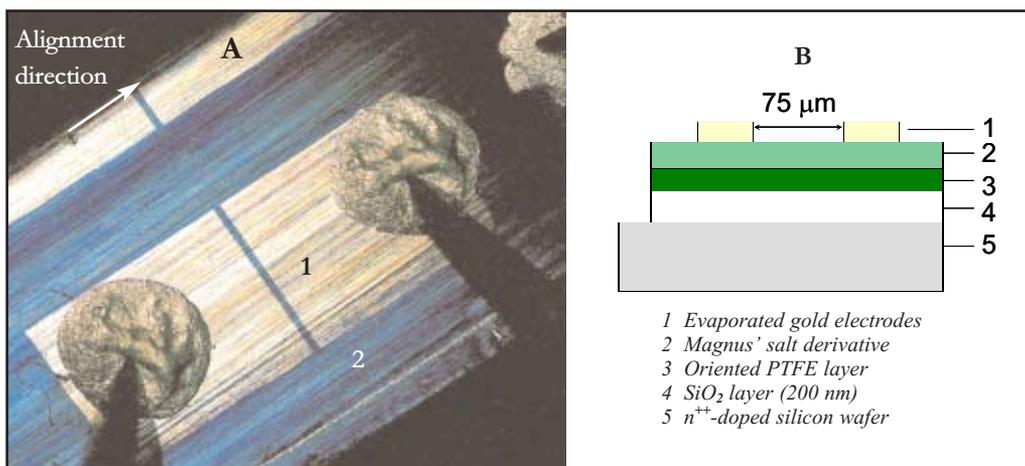


Fig. 6 Optical micrograph (A) and schematic representation (B) of a field effect transistor with an aligned  $[\text{Pt}(\text{NH}_2\text{dmoc})_4][\text{PtCl}_4]$  film

close to the optimum value that could be achieved in a DC-device structure for a well-organised layer of a semiconductor between the electrodes. Well-aligned, defect-free layers of  $[\text{Pt}(\text{NH}_2\text{dmoc})_4][\text{PtCl}_4]$  would therefore approach mobilities of  $\sim 0.1 \text{ cm}^2 \text{ Vs}^{-1}$ . It appears that Magnus' salt derivatives can be capable of sustaining attractive current densities and switching times.

Field effect transistors (FETs) that have  $[\text{Pt}(\text{NH}_2\text{dmoc})_4][\text{PtCl}_4]$  as the active semiconductor layer were produced under ambient conditions in air, both with highly oriented films grown onto PTFE orientated layers, see Figure 6, and with isotropic, spin-coated films of the Magnus' salt derivative (76). Devices in which the platinum arrays were aligned parallel to the current transport direction exhibited (*p*-type) transistor action with field effect mobilities of the order of  $10^{-3}$ – $10^{-4} \text{ cm}^2 \text{ Vs}^{-1}$ . In contrast to the more microscopic PR-TRMC measurements, the mobility observed in FET devices is still most likely to be limited by transport in disordered regions of the film, presumably in the grain boundaries. In as-prepared devices, the relatively high film-conductivity of the order of  $10^{-7} \text{ S cm}^{-1}$  limited the ON-OFF current ratio of the transistors to less than 10. While unprotected FETs comprising an organic polymer or oligomer, under current scrutiny for FETs, appear typically to suffer from degradation upon exposure to oxygen and water, the transistors with

$[\text{Pt}(\text{NH}_2\text{dmoc})_4][\text{PtCl}_4]$  did not significantly degrade, even after immersion in water at a temperature of  $90^\circ\text{C}$  for a period of 12 hours. Charge carrier mobilities in devices with the channel perpendicular to the oriented  $[\text{Pt}(\text{NH}_2\text{dmoc})_4][\text{PtCl}_4]$  molecules or in devices containing an isotropic  $[\text{Pt}(\text{NH}_2\text{dmoc})_4][\text{PtCl}_4]$  layer produced by spin-coating were two or three orders of magnitude lower than the above values in the oriented state, respectively. It is thus essential to control the structural order in the active semiconductor layer. This is easily achieved for  $[\text{Pt}(\text{NH}_2\text{dmoc})_4][\text{PtCl}_4]$ .

The simple synthesis of Magnus' salt derivatives, convenient processibility of soluble compounds of the type  $[\text{Pt}(\text{NH}_2\text{R})_4][\text{PtCl}_4]$ , and outstanding resistance to relatively harsh environmental conditions could render Magnus' salt derivatives suited for mass-produced electronic products. Note that in spite of the presence of platinum, the cost of the principal starting material for Magnus' salt derivatives has been estimated to be about only one-fifth of that of substituted poly(phenylene vinylenes) and pentacene which are among those species being considered for the preparation of "plastic electronics".

## Conclusions

Soluble and thus processible derivatives of Magnus' green salt can be obtained by substitution of ammonia by linear and branched 1-aminoalka-

nes. The quasi-one-dimensional structures of the corresponding Magnus' salts are believed to arise mainly as a consequence of electrostatic attraction between the oppositely charged coordination units, although packing effects of the aminoalkanes also appear to be of importance. In addition, weak but noteworthy interactions between adjacent platinum atoms can also appear. These are reflected in the colour of the various complexes, as well as in their electrical conductivity and in their UV and IR spectra. The compounds with comparably short Pt-Pt spacings are green, semiconducting, and display a UV band around 300 nm, which is due to a  $d_{z^2}-p_z$  transition between platinum atoms of adjacent coordination units, and a Pt-Cl stretching vibration well below  $320\text{ cm}^{-1}$ . A comparably long spacing between adjacent platinum atoms is accompanied by a pink colour of the related complexes and a Pt-Cl stretching vibration close to  $320\text{ cm}^{-1}$ .

The Pt-Pt distances in the complexes with branched aminoalkanes,  $[\text{Pt}(\text{NH}_2\text{eh})_4][\text{PtCl}_4]$  and  $[\text{Pt}(\text{NH}_2\text{dmoc})_4][\text{PtCl}_4]$ , appear to be considerably shorter than those in corresponding compounds with linear alkyl groups. The 1-amino-2-ethylhexyl derivative is amorphous, cryochromic and in solution forms supramolecular structures which contain hundreds of platinum atoms. The complex  $[\text{Pt}(\text{NH}_2\text{dmoc})_4][\text{PtCl}_4]$  is green with a particularly short Pt-Pt distance of  $3.1\text{ \AA}$  and besides the colour also shows the semiconducting properties of Magnus' green salt. It displays electrical (semiconductor) conductivity of  $1.6 \times 10^{-7}\text{ S cm}^{-1}$  at room temperature and a thermal activation energy of the conduction process of  $0.24\text{ eV}$ .

The derivatives with the optically active dmoc as well as with (R)-2-ethylhexyl exhibit circular dichroism in the region of the  $d_{z^2}-p_z$  transition. Interestingly, a bisignate Cotton effect arises, suggesting  $[\text{Pt}(\text{NH}_2\text{R})_4][\text{PtCl}_4]$  has a helical structure. The absolute values of the chiral anisotropy factors are of the order of 0.1, which is among the highest values reported for metal complexes.

Oriented fibres could be prepared for all soluble Magnus' salt derivatives. Related films of  $[\text{Pt}(\text{NH}_2\text{dmoc})_4][\text{PtCl}_4]$  can function as the active semiconducting layer in, for instance, FETs.

Remarkably, such devices show a stability towards air and water which is superior to that of unprotected FETs with typical organic polymers. Hence, Magnus' salt derivatives may pave the way for mass-produced "plastic electronics".

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## References

- 1 G. Magnus, *Pogg. Ann.*, 1828, 14, 239
- 2 G. Magnus, *Ann. Chim. Phys. Sér. 2*, 1829, 40, 110
- 3 J. Gros, *Ann. Pharm.*, 1838, 27, 241
- 4 J. Reiset, *Compt. Rend. Acad. Sci.*, 1840, 10, 870
- 5 J. Reiset, *Ann. Chim. Phys., Sér. 3*, 1844, 11, 417
- 6 F. W. Clarke and M. E. Owens, *Am. Chem. J.*, 1881, 3, 350
- 7 M. L. Rodgers and D. S. Martin, *Polyhedron*, 1987, 6, 225
- 8 D. S. Martin, R. M. Rush, R. F. Kroening and P. E. Fanwick, *Inorg. Chem.*, 1973, 12, 301
- 9 M. Peyrone, *Ann. Chem. Pharm.*, 1844, 51, 1
- 10 S. Yamada, *J. Am. Chem. Soc.*, 1951, 73, 1579
- 11 V. H. Houlding and A. J. Frank, *Inorg. Chem.*, 1985, 24, 3664
- 12 K. Honda, K. Chiba, E. Tsuchida and A. J. Frank, *J. Mater. Sci. Lett.*, 1989, 24, 4004
- 13 V. A. Palkin, T. A. Kuzina, N. N. Kuz'mina and R. N. Shchelokov, *Zh. Neorg. Khim.*, 1980, 25, 1291; Engl. transl. *Russ. J. Inorg. Chem.*, 1980, 25, 720
- 14 V. A. Palkin, N. N. Kuz'mina and I. I. Chernyaev, *Zh. Neorg. Khim.*, 1965, 10, 41; Engl. transl. *Russ. J. Inorg. Chem.*, 1965, 10, 23
- 15 M. Peyrone, *Ann. Chim. Phys. Sér. 3*, 1844, 12, 193
- 16 J. Reiset, *J. Prakt. Chem.*, 1844, 33, 21
- 17 J. Reiset, *Compt. Rend. Acad. Sci.*, 1844, 18, 1100
- 18 J. Reiset, *Ann. Chim.*, 1845, (no volume), 161
- 19 C. Gerhardt, *Compt. Rend. Acad. Sci.*, 1850, 31, 241
- 20 C. Gerhardt, *J. Prakt. Chem.*, 1851, 53, 345
- 21 J. Liebig and F. Wöhler (eds.), "Jahresber. Fortschritte Rein. Pharm. Techn. Chem. Phys. Mineral. Geol.", 1850, (no volume), 335
- 22 J. Liebig and H. Kopp (eds.), "Jahresber. Fortschritte Rein. Pharm. Techn. Chem. Phys. Mineral. Geol.", 1856, (no volume), 413
- 23 F. Wöhler and J. Liebig (eds.), *Ann. Chem. Pharm.*, 1850, 76, 307
- 24 S. M. Jörgensen, *J. Prakt. Chem.*, 1886, 141, 489

- 25 S. M. Jørgensen and S. P. L. Sørensen, *Z. Anorg. Chem.*, 1906, 48, 441
- 26 A. Hantzsch and F. Z. Rosenblatt, *Z. Anorg. Allg. Chem.*, 1930, 187, 241
- 27 M. Atoji, J. W. Richardson and R. E. Rundle, *J. Am. Chem. Soc.*, 1957, 79, 3017
- 28 T. Yoshida, T. Yamagata, T. H. Tulip, J. A. Ibers and S. Otsuka, *J. Am. Chem. Soc.*, 1978, 100, 1064
- 29 P. Braunstein, J.-M. Jud, Y. Dusausoy and J. Fischer, *Organometallics*, 1983, 2, 180
- 30 A. A. Frew, R. H. Hill, L. Manojlovic-Muir, K. W. Muir and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1982, 198
- 31 R. J. Goodfellow, I. R. Herbert and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1983, 1386
- 32 M. P. Brown, R. J. Puddephatt, M. Rashidi, L. Manojlovic-Muir, K. W. Muir, T. Solomun and K. R. Seddon, *Inorg. Chim. Acta*, 1977, 23, L33
- 33 M. Ciriano, J. A. K. Howard, J. L. Spencer, F. G. A. Stone and H. Wadepohl, *J. Chem. Soc., Dalton Trans.*, 1979, 1749
- 34 A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1975, 1516
- 35 N. J. Taylor, P. C. Chieh and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 1975, 448
- 36 L. V. Interrante and R. P. Messmer, *Inorg. Chem.*, 1971, 10, 1175
- 37 J. R. Miller, *J. Chem. Soc.*, 1961, 4452
- 38 D.-M. Peyrone, *Ann. Chim. Phys. Sér. 3*, 1846, 16, 462
- 39 G. C. Wittstein, *Repertorium Pharm.*, 1848, 100, 456
- 40 Vauquelin, *Ann. Chim. Sér. 2*, 1817, 5, 260
- 41 Vauquelin, *Ann. Chim. Sér. 2*, 1817, 5, 392
- 42 E. Hertel and K. Schneider, *Z. Anorg. Allg. Chem.*, 1931, 202, 77
- 43 J. Breimi, D. Brovelli, W. Caseri, G. Hähner, P. Smith and T. Tervoort, *Chem. Mater.*, 1999, 11, 977
- 44 J. Breimi, V. Gramlich, W. Caseri and P. Smith, *Inorg. Chim. Acta*, 2001, 322, 23
- 45 M. Fontana, H. Chanzy, W. R. Caseri, P. Smith, A. P. H. J. Schenning, E. W. Meijer and F. Gröhn, *Chem. Mater.*, 2002, 14, 1730
- 46 S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Jpn.*, 1958, 31, 813
- 47 A. Wurtz, *Ann. Chim. Phys. Sér. 3*, 1850, 30, 443
- 48 J. R. Miller, *Proc. Chem. Soc.*, 1960, 318
- 49 M. E. Cradwick, D. Hall and R. K. Phillips, *Acta Cryst. B*, 1971, 27, 480
- 50 L. Tschugaëff, *Ber. Deutsch. Chem. Ges.*, 1907, 40, 173
- 51 J. R. Miller, *J. Chem. Soc.*, 1965, 713
- 52 C. Gordon, *Ber. Deutsch. Chem. Ges.*, 1870, 3, 174
- 53 J. Breimi, W. Caseri and P. Smith, *J. Mater. Chem.*, 2001, 11, 2593
- 54 P. Day, A. F. Orchard, A. J. Thomson and R. J. P. Williams, *J. Chem. Phys.*, 1965, 42, 1973
- 55 B. G. Anex, M. E. Ross and M. W. Hedgcock, *J. Chem. Phys.*, 1967, 46, 1090
- 56 M. Fontana, W. R. Caseri, P. Smith, A. P. H. J. Schenning and E. W. Meijer, *Inorg. Chim. Acta*, 2003, 353, 320
- 57 A. Rodger, *Inorg. Chim. Acta*, 1986, 122, 25
- 58 C. Munir, N. Ahmad, A. S. Alam and M. Danish, *Arab. J. Sci. Eng.*, 1994, 19, 509
- 59 O. P. Slyudkin, M. A. Kerzhentsev, I. S. Slyudkina and L. M. Volshtein, *Zh. Neorg. Khim.*, 1977, 22, 3299; Engl. transl. *Russ. J. Inorg. Chem.*, 1977, 22, 1798
- 60 R. D. Peacock and B. Stewart, *Coord. Chem. Rev.*, 1982, 46, 129
- 61 O. P. Slyudkin, *Zh. Neorg. Khim.*, 1983, 28, 2300; Engl. transl. *Russ. J. Inorg. Chem.*, 1983, 28, 1303
- 62 R. Saito and Y. Kidani, *Bull. Chem. Soc. Jpn.*, 1983, 56, 449
- 63 R. Saito and Y. Kidani, *Bull. Chem. Soc. Jpn.*, 1984, 57, 3430
- 64 C. J. Hawkins and J. Martin, *Inorg. Chem.*, 1982, 21, 1074
- 65 G. M. Summa and B. A. Scott, *Inorg. Chem.*, 1980, 19, 1079
- 66 C. N. R. Rao and S. N. Bhat, *Inorg. Nucl. Chem. Lett.*, 1969, 5, 531
- 67 L. V. Interrante, *J. Chem. Soc., Chem. Commun.*, 1972, 302
- 68 P. S. Gomm, T. W. Thomas and A. E. Underhill, *J. Chem. Soc. A*, 1971, 2154
- 69 F. Mehran and B. A. Scott, *Phys. Rev. Lett.*, 1973, 31, 99
- 70 L. V. Interrante, *Adv. Chem. Ser.*, 1976, 150, 1
- 71 F. Mehran and L. V. Interrante, *Solid State Commun.*, 1976, 18, 1031
- 72 R. Kubota, H. Kobayashi, L. Tsujikawa and T. Enoki, *Int. J. Quantum Rev.*, 1980, 18, 1533
- 73 M. Tanaka, N. Kojima, Y. Ajiro, T. Ban and I. Tsujikawa, *Synth. Met.*, 1987, 19, 967
- 74 Raewsky, *Compt. Rend. Acad. Sci.*, 1847, 25, 794
- 75 M. Fontana, H. Chanzy, N. Stutzmann, W. R. Caseri and P. Smith, *Thin Solid Films*, 2004, 449, 34
- 76 W. R. Caseri, H. D. Chanzy, K. Feldman, M. Fontana, P. Smith, T. A. Tervoort, J. G. P. Goossens, E. W. Meijer, A. P. H. J. Schenning, I. P. Dolbnya, M. G. Debije, M. P. de Haas, J. M. Warman, A. M. van de Craats, R. H. Friend, H. Siringhaus and N. Stutzmann, *Adv. Mater.*, 2003, 15, 125
- 77 J.-C. Wittmann and P. Smith, *Nature*, 1991, 352, 414
- 78 P. G. Schouten, J. M. Warman and M. P. de Haas, *J. Phys. Chem.*, 1993, 97, 9863
- 79 G. H. Gelinck and J. M. Warman, *J. Phys. Chem.*, 1996, 100, 20035

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