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Polymeric Quasi-one-dimensional Platinum Compounds

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Summary: Magnus' green salt, $[Pt(NH_3)_4][PtCl_4]$, is a quasi-one-dimensional inorganic semiconductor containing linear arrays of platinum atoms. Its use in materials science is limited since it does not melt prior to decomposition and is largely insoluble in water and organic solvents which makes processing difficult. We have remedied this deficiency by substitution of coordinated ammonia or chloride by monodentate or bidentate ligands, including optically active aminoalkanes, resulting in soluble compounds. Depending on the ligands, the polymeric supramolecular structure in the solid state persisted in solution or decayed to ion pairs. In the solid state, the ligands markedly influenced the Pt-Pt distances, which on their part directed optical and electrical properties. Thus, high chiral anisotropy factors, cryochromic behavior, or (anisotropic) electric semiconductivity were found. A number of derivatives were processed to oriented films and fibers. Some complexes exhibited the color and electric characteristics of Magnus' green salt and thus can be regarded as soluble equivalents of Magnus' green salt. Oriented films of such a compound were applied as active semiconducting layer in field-effect transistors (FET). The corresponding devices showed remarkable stability towards air and water which was superior to that of unprotected field-effect transistors based on typical organic polymers.

Keywords: fibers; magnus' salts; oriented films; platinum; semiconductors

Introduction

Quasi-one-dimensional inorganic compounds have found wide attention not only for their structural constitution but also for their materials properties, in particular their electric conductivity.[1,2] One of the first of these compounds was synthesized around 1830 by Gustav Magnus.[3,4] He dissolved $PtCl_2$ in an aqueous solution of hydrochloric acid, whereupon $[PtCl_4]^{2-}$ formed in situ. By addition of ammonia, a part of the $[PtCl_4]^{2-}$ converted to $[Pt(NH_3)_4]^{2+}$ which yielded, together with $[PtCl_4]^{2-}$ which had not reacted yet with ammonia, a green complex of the composition $[Pt(NH_3)_4][PtCl_4]$. This substance has been known rapidly as Magnus' green salt. Although its chemical composition was analyzed correctly already by Magnus, its detailed constitution became evident only when X-ray diffraction analysis became available. Thus, alternately stacked square planar $[Pt(NH_3)_4)]^{2+}$ and $[PtCl_4]^{2-}$ moieties were detected, resulting in a structure which corresponds to that of a rigid polymer comprising linear arrays of platinum atoms (Figure 1). These platinum atoms are separated by 3.25 Å,[1] which is significantly larger than the typical Pt–Pt bond lengths of 2.6–2.8 Å. As a consequence, it was concluded that electrostatic interactions between the oppositely charged coordination units play a dominant role in the formation of the quasi-one-dimensional structure, rather than Pt–Pt bonds, although weak interactions between adjacent platinum atoms still exist.[5,6] Hence, Magnus' green salt can be regarded

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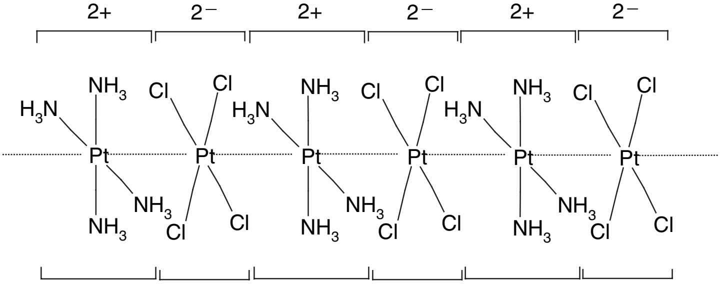

Figure 1.
Schematic illustration of the quasi-one-dimensional structure of Magnus' green salt.

as a polymeric supramolecular compound where the constitutional repeat units are not linked covalently but electrostatically. In the course of time, a considerable number of complexes have been derived from Magnus' green salt, composed of the general formula $[PtL_4]^{2+}[PtL'_4]^{2-}$ (L and L′ are ligands or coordinating parts of multidentate ligands); as summarized recently in the literature.[7] The complexes which were subjected to X-ray analysis revealed a linear backbone of platinum atoms with typical Pt–Pt distances of 3.2–3.6 Å, depending on the ligands.[7,8] A systematic dependence of the Pt–Pt distance on the nature of the ligands has not been found yet.

Since Magnus' green salt and some of its derivatives prepared previously show properties such as dichroism[6,9–15] or anisotropic electrical semiconductivity,[16–22] they appear to be attractive for materials science, all the more Magnus' green salt itself is notably stable towards heat, acidic and alkaline solutions.[23] However, Magnus' green salt and the complexes derived thereof as described in the literature are typically insoluble in common solvents and do not melt without decomposition which markedly limits their usage. Further, it was not evident if the polymeric structure is mainly a result of the crystal packing or if polymeric characteristics can also arise in the dissolved state. In the last years, however, we succeeded in the preparation of soluble and processible derivatives of Magnus' green salt, and the corresponding complexes as well as their properties are summarized and supplemented in the following.

Magnus' Salt Derivatives with Linear 1-aminoalkanes

Since Magnus' green salt shows the structural attribute of a rigid-rod polymer, it is anticipated that characteristic properties of this class of polymers are also symptomatic to Magnus' green salt. Rigid-rod polymers are commonly insoluble and decompose prior to melting, which is indeed valid also for Magnus' green salt. It has been established in the last decades, however, that solubility of rigid-rod polymers can be enabled by binding flexible side groups to the rigid main chain.[24–26] We attempted to apply this concept also to Magnus' salt structures. For this purpose, the most simple strategy appeared to be the substitution of ammonia by 1-aminoalkanes. Since complexes of the type $[Pt(NH_2R)_4][PtCl_4]$ with R representing a methyl, ethyl, propyl or butyl group, which were described already 100–150 years ago,[13,27–29] are still insoluble in common solvents, we explored compounds with longer alkyl chains ranging from heptyl to tetradecyl. [30] In order to synthesize these substances, $[PtCl_4]^{2-}$ was first converted in solution by addition of NH_2R to $[Pt(NH_2R)_4]^{2+}$, and this cation was subsequently treated in situ with $[PtCl_4]^{2-}$ whereupon the desired compounds formed. Indeed, the resulting Magnus' salt derivatives were soluble in hot chloroform and those with alkyl groups longer than heptane also in hot tetrahydrofuran, toluene and *p*-xylene. Upon cooling of solutions above a concentration of ca. 0.1–0.5% w/w to room temperature, gels emerged which were stable at least for months. Optical microscope images of gels placed between crossed polarizers revealed birefringent, highly ordered, fibrillar structures. The birefringence was lost when the gels were heated to adopt the fluid state again. Importantly, the dried gels dissolved again at elevated temperatures under loss of birefringence, and birefringent gels arose once more upon cooling to room temperature, indicating that the gelation process was thermally reversible and associated with an ordering or crystallization process. Gels of the 1-aminooctane derivative were used for the preparation of oriented fibers by electrostatic spinning and films by mechanical stretching; the orientation was established by turning the objects between crossed polarizers.

While Magnus' green salt acts as a semiconductor, the conductivity of the soluble derivatives with 1-aminoalkane ligands fell rather in the range of insulators. In fact, the latter platinum compounds were pink which indicates that interactions between adjacent platinum atoms are weak or absent and that the Pt–Pt distances are considerably larger than in the green compounds.[30] In fact, from the compounds with linear 1-aminoalkanes known previously, only the aminomethane derivative shows a green color,[6,14,27,28,31] and accordingly its Pt–Pt distance corresponds to that of Magnus' green salt.[9,32] All other complexes with linear 1-aminoalkanes are, however, pink (or reddish)[6,14,30,32] (brown or greenish-grey modifications mentioned in old reports[27–29] are considered not to consist of (pure) Magnus' salt derivatives[30]). Notably, in the pink aminoethane derivative which shows a Pt–Pt distance of 3.62 Å, the coordination plane of the tetrakis(aminoethane)platinum(II) unit is inclined by 29° to that of the tetrachloroplatinate(II) plane,[32] indicating that not only electrostatic attractions but also crystal packing effects determine the Pt–Pt distance.

Magnus' Salt Derivatives with Branched 1-aminoalkanes

When branched instead of linear 1-aminoalkane ligands are applied, the above conclusions suggest that the crystal packing and thus the Pt–Pt distance with the associated materials properties might change. In order to test this hypothesis, NH_2R ligands with the alkyl residues (*S*)-3,7-dimethyloctyl (dmoc) and 2-ethylhexyl (eh) were explored.[8,33–38] Indeed, the compounds $[Pt(NH_2dmoc)_4][PtCl_4]$, $[Pt(NH_2dmoc)_4][PtBr_4]$ and $[Pt(NH_2eh)_4][PtCl_4]$ differed already in color from the counterparts with linear 1-aminoalkanes of similar chain lengths. The two NH_2dmoc derivatives were green and crystalline while the NH_2eh derivative was amorphous and dark violet (or greyish, probably depending on the surface roughness of the solids or differences in light reflection) at room temperature. Remarkably, however, the NH_2eh derivative showed upon cooling a reversible color change to green at ca. −55 °C (the pink derivatives with linear 1-aminoalkanes kept their color at least down to −196 °C). Differential scanning calorimetric (DSC) traces did not reveal a pronounced energy change in the temperature region of the color change. Also, there was no indication from X-ray diffraction patterns that the Pt–Pt distance changed abruptly around −55 °C. Hence, relatively small structural changes seem to induce the sudden color change.

Powder diffraction studies of the NH_2dmoc and the NH_2eh derivatives suggested Pt–Pt distances of 3.1–3.2 Å, i.e. in the range or even somewhat shorter than that in Magnus' green salt although it has been claimed earlier[14] that aminoalkanes with at least two carbon atoms yield pink Magnus' salt derivatives due to a relatively long Pt–Pt distance as a result of the packing of the alkyl groups. The short Pt–Pt distances in the derivatives with the branched alkyl groups seem to be reflected also in UV and IR spectra.[10,30] The Pt–Cl stretching vibrations of the compounds with the linear alkyl groups emerged around 320 cm^{-1} which is close to the value of $K_2[PtCl_4]$ but significantly higher than that of Magnus' green salt (at 311 cm^{-1}), $[Pt(NH_2eh)_4][PtCl_4]$ (at 306 cm^{-1}) and $[Pt(NH_2dmoc)_4][PtCl_4]$ (at 303 cm^{-1}). Also, the Pt–Br stretching vibration of $[Pt(NH_2dmoc)_4][PtBr_4]$ at 223 cm^{-1} arose below the related frequency of $K_2[PtBr_4]$ (233 cm^{-1}). The UV/vis absorption spectra of solid Magnus' green salt, the green aminomethane,[15] the NH_2eh and the two NH_2dmoc derivatives were dominated in the wavelength range of 200–800 nm by a band at 290–310 nm which is not characteristic for the pink compounds. For Magnus' green salt, this absorption maximum was attributed to a transition of the d_z2 orbital of the $[PtCl_4]^{2-}$ to the p_z orbital of the $[Pt(NH_3)_4]^{2+}$ unit,[9] which, of course, becomes ineffective in Magnus' salt derivatives if the coordination units are separated too far from each other. This charge transfer transition was obviously involved in circular dichroism (CD) induced by the coordinated optically active aminoalkanes containing (*S*)-3,7-dimethyloctyl or (*R*)-2-ethylhexyl groups. CD spectra of solid $[Pt(NH_2dmoc)_4][PtCl_4]$ and $[Pt(NH_2eh)_4][PtCl_4]$ revealed strong signals in the region of 300 nm (an example is shown in Figure 2, which also includes the related UV spectrum). Surprisingly, a *bisignate* Cotton effect emerged for both complexes, 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), which indicates a strong exciton coupling between the chromophores. In organic structures, a bisignate Cotton effect is commonly associated with a helical arrangement of the chromophores, whereas the negative sign of the first and the positive sign of the second Cotton effect implies a left-handed screwness of the electric transition dipole moments of the neighboring chromophores. One should be aware, however, that CD spectra of metal complexes arise rather as a result of the chirality of the metal-ligand system as a whole than of the individual chromophores. [39] Therefore, the CD spectra of the NH_2dmoc and NH_2eh derivatives do not necessarily point to a helical structure of the platinum backbone. Besides the bisignate Cotton effect itself, the chiral anisotropy factors (g_{abs}) also attracted attention since they were extraordinarily high for both the NH_2dmoc and the NH_2eh derivative (0.10–0.12).

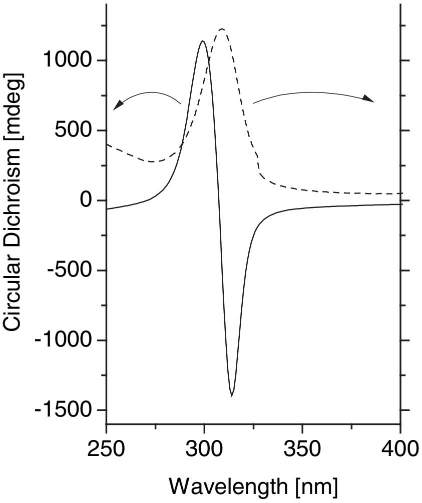

Figure 2.
Circular dichroism (CD, solid line) and UV spectrum (dashed line) of $[Pt(NH_2dmoc)_4][PtCl_4]$.

The complexes $[Pt(NH_2dmoc)_4][PtCl_4]$, $[Pt(NH_2dmoc)_4][PtBr_4]$ and $[Pt(NH_2eh)_4]$-$[PtCl_4]$ were soluble in hot organic solvents without decomposition. In order to determine the molecular weight of the NH_2eh-derivative in solution, the latter was subjected to membrane osmometry in the concentration range of 0.1–1.0% w/w in toluene at a temperature of 37 °C. The investigations pointed at a number average molecular weight (M_n) of $4 \cdot 10^5$ g/mol, which corresponds to an assembly with ca. 750 platinum atoms. It appears therefore that supramolecular structures of $[Pt(NH_2eh)_4]^{2+}$ and $[PtCl_4]^{2-}$ units can form not only in the solid state but also in solution, most likely caused by electrostatic attraction between the oppositely charged coordination units.

As in the case of the Magnus' salt derivatives with linear 1-aminoalkanes, fibers of $[Pt(NH_2dmoc)_4][PtCl_4]$ and $[Pt(NH_2eh)_4][PtCl_4]$ were produced by electrostatic spinning and films of these two complexes as well as of $[Pt(NH_2eh)_4]$-$[PtBr_4]$ by deposition of the compounds from super-saturated solutions onto glass slides covered with a thin layer of highly oriented poly(tetrafluoroethene) (PTFE), which was previously deposited on the slides by friction deposition at elevated temperature.[40] The Magnus' salt derivatives in the fibers and films were oriented as evident from polarization microscopy and in the case of $[Pt(NH_2dmoc)_4][PtCl_4]$ also from transmission electron microscopy (TEM), atomic force microscopy (AFM) and electron diffraction. Orientation of $[Pt(NH_2dmoc)_4][PtCl_4]$, $[Pt(NH_2dmoc)_4]$-$[PtBr_4]$ and $[Pt(NH_2eh)_4][PtCl_4]$ in the films was also confirmed by UV/vis absorption spectra recorded with polarized light (Figure 3). At parallel orientation of the polarization plane with respect to the platinum arrays, the absorption maxima (310 nm for the NH_2dmoc and 300 nm for the NH_2eh derivatives) were clearly more pronounced than at perpendicular orientation.

The bulk electrical conductivity of pressed samples of $[Pt(NH_2dmoc)_4][PtCl_4]$, $[Pt(NH_2dmoc)_4][PtBr_4]$ and $[Pt(NH_2eh)_4]$-$[PtCl_4]$ amounted roughly to 10^{-7} S/cm, 10^{-8} S/cm and 10^{-10} S/cm, respectively, at room temperature. For comparison, pressed samples of Magnus' green salt measured under similar conditions showed a conductivity of $5 \cdot 10^{-6}$ S/cm. In the case of $[Pt(NH_2dmoc)_4][PtCl_4]$, the temperature dependence of the conductivity was also investigated. It followed the expression

$$\ln\frac{\sigma}{\sigma_0} = -\frac{E_a}{k_B T}$$

with σ the electrical conductivity, σ_0 an arbitrary constant (conveniently 1 S/cm), E_a the activation energy, k_B Boltzmann's constant, and T the absolute temperature. This temperature dependence is characteristic for semiconductors with a single thermally activated conduction process in the observed temperature interval.[21] Indeed, a logarithmic representation of the conductivity versus the inverse temperature resulted in a straight line (Figure 4). 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).[18–21] In oriented films of $[Pt(NH_2dmoc)_4][PtCl_4]$, the conductivity was several orders of magnitude higher parallel to the platinum arrays (10^{-4}–10^{-3} S/cm) than perpendicular (ca. 10^{-8} S/cm) to them. These differences were less pronounced in $[Pt(NH_2dmoc)_4][PtBr_4]$

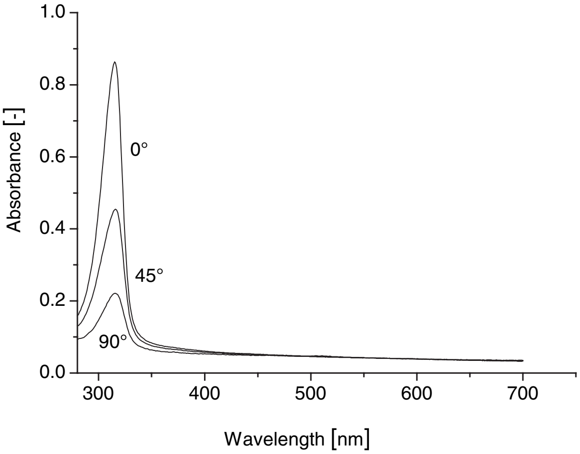

Figure 3.
Polarized UV/vis spectrum of an uniaxially oriented film of $[Pt(NH_2dmoc)_4][PtCl_4]$ at different angles between the polarization plane of the incident light and the orientation direction of the film.

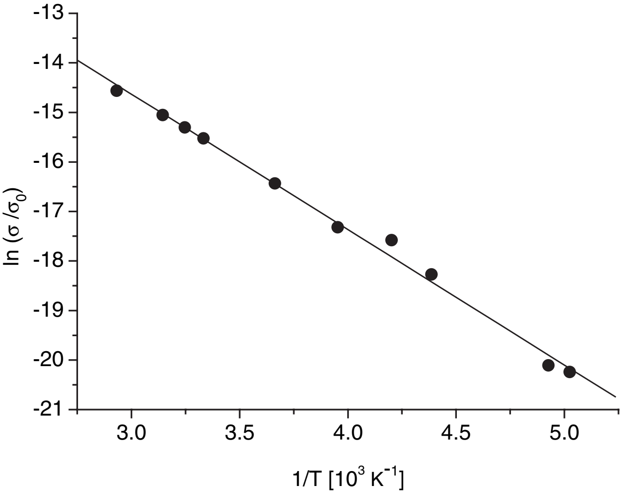

Figure 4.
Relation between the conductivity (σ) of a pressed sample of $[Pt(NH_2dmoc)_4][PtCl_4]$ and the temperature (T), with $\sigma_0 = 1$ S/cm.

(ca. 10^{-7} S/cm and 10^{-9} S/cm, respectively) and $[Pt(NH_2eh)_4][PtCl_4]$ (ca. 10^{-8} S/cm and $8 \cdot 10^{-10}$ S/cm, respectively). The anisotropic conductivities are consistent with a charge mobility along the arrays of platinum atoms. The intrinsic mobility of charge carriers in $[Pt(NH_2dmoc)_4][PtCl_4]$, determined with the pulse-radiolysis time-resolved microwave conductivity technique (PR-TRMC), was 0.06 $cm^2/(Vs)$,[36] which compares favorably with values found for π-stacked discotic materials and π-bond conjugated polymers.[41,42] Charge carrier mobilities in devices with the channel oriented perpendicular to the platinum arrays in $[Pt(NH_2dmoc)_4][PtCl_4]$ films or in devices made with an isotropic $[Pt(NH_2dmoc)_4][PtCl_4]$ layer prepared by spin-coating were two or three orders of magnitude lower than the values in the oriented parallel state. Thus, it is of importance to control the structural order for electronic applications in which $[Pt(NH_2dmoc)_4][PtCl_4]$ acts as an active semiconductor layer, e.g. in field-effect transistors (FETs). Such devices were produced under ambient conditions in air, both with highly oriented and isotropic films of the dmoc derivative.[36] Devices with the platinum arrays oriented parallel to the current transport direction showed (p-type) transistor action with field-effect mobilities on the order of 10^{-3}–10^{-4} $cm^2/(Vs)$. In contrast to the more microscopic PR-TRMC measurements, the mobilities observed in FETs are most likely limited by transport in disordered regions of the film, probably mainly grain boundaries. It is worth to note that unprotected field-effect transistors on the basis of organic polymers and oligomers that are actually considered for FETs are commonly sensitive to degradation upon contact with oxygen and water. The FETs with $[Pt(NH_2dmoc)_4]$-$[PtCl_4]$, however, were not affected significantly in air and not even upon immersion in hot water at 90 °C for a period of 12 h. Thus, it appears that the simple synthesis of soluble Magnus' salt derivatives, their convenient processibility and outstanding resistance to relatively harsh environmental conditions could render such complexes suited for mass-produced electronic products.

Magnus' Salt Derivatives with Bidentate Ligands

The chloride ions or ammonia molecules in Magnus' green salt were also substituted by bidentate dianionic or neutral ligands,

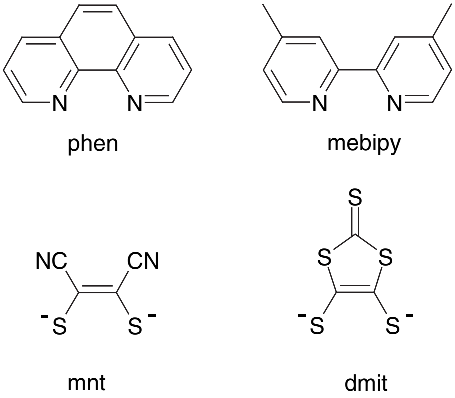

Figure 5.
Structure and acronyms of bidentate ligands employed in Magnus' salt derivatives.

respectively. Besides structural characteristics of the resulting Magnus' salt derivatives, bidentate ligands might in particular improve the thermal stability of the platinum complexes. As an example, maleodintriledithiolate (mnt, Figure 5) was selected as a bidentate ligand. In complexes with this ligand, the negative charges are not strictly fixed at the sulfur atoms but, to some extent, delocalized over the entire coordination unit.[43] The complex $[Pt(NH_2oc)_4]$-$[Pt(mnt)_2]$, with oc denoting octyl, was prepared by combination of $(Nbu_4)_2[Pt$-$(mnt)_2]$ (bu = butyl) and $[Pt(NH_2oc)_4]$-Cl_2.[44] X-ray single crystal structure analysis revealed, unusually, two different Pt–Pt distances (3.86 Å and 4.01 Å) which emerged in alternating sequence. These distances are large compared to those of Magnus' green salt and most of its derivatives reported so far. The complex was soluble at room temperature, for instance, in acetone or acetonitrile. Results from vapor phase osmometry in acetone suggested that the compound was present as an ion pair. Due to the versatile redox chemistry of Pt-mnt complexes, a relatively high electric conductivity was surmised in $[Pt(NH_2oc)_4][Pt(mnt)_2]$. However, this quantity was below 10^{-9} S/cm. Since the electric conductivity in conjugated organic polymers is frequently enhanced by oxidation with iodine, this procedure was also applied to $[Pt(NH_2oc)_4][Pt(mnt)_2]$. Indeed, oxidation took place but the resulting complex $[Pt(NH_2oc)_4][Pt(mnt)_2]_2$, in which the platinum atoms in the $[Pt(mnt)_2]^-$ units were present in the uncommon oxidation state III, did not comprise linear arrays of platinum atoms anymore, as evident from X-ray structure analysis, and noteworthy electric conductivity was not found.[45]

While the onset of decomposition in the above discussed Magnus' salt derivatives was below 200 °C, higher thermal stability was achieved when bidentate ligands were used both in the anionic and the cationic coordination unit since complexes with bidentate ligands generally show increased stability. Besides mnt, 1,3-dithiol-2-thione-4,5-dithiolate (dmit) was used as an anion, and 1,10-phenanthroline (phen) and 4,4′-dimethyl-2,2′-dipyridyl (mebipy) as neutral bidentate ligands (Figure 5).[46] When UV/vis absorption spectra of the resulting compounds $[Pt(phen)_2][Pt(mnt)_2]$, $[Pt(mebipy)_2][Pt(mnt)_2]$, $[Pt(phen)_2][Pt(dmit)_2]$, $[Pt(mebipy)_2][Pt(dmit)_2]$ (in dimethyl sulfoxide) were compared with the spectra of the individual coordination units, i.e. $[Pt$-$(mebipy)_2]^{2+}$ $[Pt(phen)_2]^{2+}$, $[Pt(mnt)_2]^{2-}$ and $[Pt(dmit)_2]^{2-}$, respectively, it appeared that the spectra of the Magnus' salt derivatives were not composed of a superposition of the spectra of the individual coordination units (an example is shown in Figure 6). This may indicate an interaction of adjacent coordination units in the Magnus' salt derivatives. The absorption maxima in the UV/vis spectra originate most likely from L-L, L-M or M-L transitions.

The thermal stability of these complexes depended mainly on the anionic ligand. Decomposition of the dmit complexes began at 210–220 °C and of the mnt complexes at 300–320 °C. The compounds were insoluble in most organic solvents; solubility was found at elevated temperature (110 °C) in dimethylsulfoxide, dimethyl formamide and N-methyl pyrrolidone. Investigations with electron paramagnetic resonance (EPR) revealed unpaired electrons in the phen and mebipy

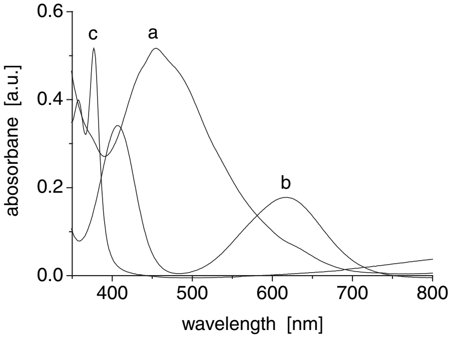

Figure 6.
UV/vis absorption spectra in dimethyl sulfoxide of (a) $[Pt(phen)_2][Pt(dmit)_2]$, (b) $(NBu_4)_2[Pt(dmit)_2]$ and (c) $[Pt(phen)_2](PF_6)_2$.

complexes, as in the case of Magnus' green salt. These unpaired electrons in the Magnus' salt derivatives were attributed to the presence of impurities or to oxidation processes, which might imply that considerable electric conductivity is expected. However, detailed analysis of the EPR investigations revealed that the unpaired electrons were located predominantly at the sulfur atoms and not at the platinum atoms. While the electric conductivity in the mnt complexes was low (ca. 10^{-10} S/cm), as in the case of $[Pt(NH_2oc)_4]$-$[Pt(mnt)_2]$, that of $[Pt(phen)_2][Pt(dmit)_2]$ amounted to $4.1 \cdot 10^{-6}$ S/cm and that of $[Pt(mebipy)_2][Pt(dmit)_2]$ to $1.4 \cdot 10^{-5}$ S/cm at room temperature. These complexes showed a linear dependence of the logarithm of the conductivity on the inverse temperature, as discussed above for $[Pt(NH_2dmoc)_4][PtCl_4]$. Remarkably, the EPR studies suggested that the conductivity in the dmit derivatives was not related to the detected paramagnetic species. The thermal activation energies for excitation of an electron from the valence band to the conductive band were 0.2 eV, which is in the range of that of Magnus' green salt and $[Pt(NH_2dmoc)_4][PtCl_4]$. Hence, $[Pt(phen)_2][Pt(dmit)_2]$ and $[Pt(mebipy)_2]$-$[Pt(dmit)_2]$ are thermally rather stable semiconductors with electronic characteristics similar to those of Magnus' green salt.

Conclusions

Soluble and thus processible derivatives of Magnus' green salt were synthesized with little effort with 1-aminoalkanes of appropriate length or of bidentate ligands. Depending on the ligand, ion pairs or polymeric structures held together by electrostatic forces existed in solution. In the solid state, not only electrostatic attraction between the oppositely charged coordination units but also packing effects determine the Pt–Pt distances. In particular, branched alkyl groups in $[Pt(NH_2R)_4]^{2+}$ units seem to complicate crystallization which favors a decrease of the interplatinum distances. Weak but significant interactions between adjacent platinum atoms arise in such derivatives, which are reflected in the color, the electrical conductivity as well as UV and IR spectra. These interactions most likely also contribute to the uncommon behavior of $[Pt(NH_2eh)_4][PtCl_4]$ which is cryochromic or to the pronounced circular dichroism of the optically active $[Pt(NH_2dmoc)_4]$-$[PtCl_4]$ and $[Pt(NH_2eh)_4][PtCl_4]$ complexes which arises in the region of the d_z2-p_z transition of adjacent platinum atoms with a bisignate Cotton effect and very high absolute values of the chiral anisotropy factors (around 0.1)

Oriented films and fibers were accessible for all soluble Magnus' salt derivatives with linear and branched 1-aminoalkanes. These films and fibers exhibit anisotropic optic and electric properties. The $[Pt(NH_2dmoc)_4][PtCl_4]$ and $[Pt(NH_2dmoc)_4]$-$[PtBr_4]$ complexes may attract particular attention because they show the color and electric characteristics of Magnus' green salt and thus can be regarded as soluble equivalents of Magnus' green salt. Oriented films of $[Pt(NH_2dmoc)_4][PtCl_4]$ were used as active semiconducting layer in field-effect transistors. The prepared devices showed a remarkable stability towards air and water which is superior to that of unprotected field-effect transistors with typical organic polymers. Since some of the Magnus' salt derivatives with bidentate ligands display higher thermal stability than derivatives with monodentate ligands and electric properties which are similar to those of Magnus' green salt, it cannot be excluded that derivatives with bidentate ligands are even better suited for electronic components than $[Pt(NH_2dmoc)_4][PtCl_4]$ or $[Pt(NH_2dmoc)_4][PtBr_4]$.

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