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A Soluble Equivalent of the Supramolecular, Quasi-One-Dimensional, Semiconducting Magnus' Green Salt

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A soluble supramolecular, quasi-one-dimensional semiconducting complex comprising alternately stacked $[Pt(NH_2dmoc)_4]^{2+}$ and $[PtCl_4]^{2-}$ units, where dmoc denotes (*S*)-3,7-dimethyloctyl, has been synthesized and characterized with various methods. In contrast to earlier enunciated expectations and unlike nearly all other known derivatives, $[Pt(NH_2dmoc)_4][PtCl_4]$ showed the color of Magnus' green salt, $[Pt(NH_3)_4][PtCl_4]$, which is characteristic for linearly arranged platinum atoms with considerable Pt−Pt interactions. The Pt−Pt distance in $[Pt(NH_2dmoc)_4][PtCl_4]$ was established to be 3.1 Å from powder X-ray and electron diffraction patterns. Similar to Magnus' green salt, $[Pt(NH_2dmoc)_4][PtCl_4]$ was found to be a semiconductor with a thermal activation energy of 0.24 eV and an electrical conductivity of 1.6×10^{-7} S/cm at room temperature. Although Magnus' green salt virtually is intractable, $[Pt(NH_2dmoc)_4][PtCl_4]$ was soluble in common organic solvents. Remarkably, strong evidence indicated that self-assembled platinum chain structures were present also in solution. Hence, $[Pt(NH_2dmoc)_4][PtCl_4]$ may indeed be regarded as a processible form of Magnus' green salt.

Introduction

Supramolecular quasi-one-dimensional structures comprising a backbone of metal atoms have found attention in particular in the field of electrical conductivity[1−5] and also in the areas of low-dimensional magnetism[6,7] and nonlinear optics.[8,9] One of the most investigated among such compounds is Magnus' green salt, $[Pt(NH_3)_4][PtCl_4]$ (Figure 1), which was first synthesized and correctly chemically analyzed almost 200 years ago.[10,11] X-ray crystal structure analysis revealed that the structure of Magnus' green salt involves a backbone of linearly arranged platinum atoms separated by 3.23−3.25 Å.[12−14] The formation of the supramolecular arrangement is a result mainly of electrostatic attraction between the

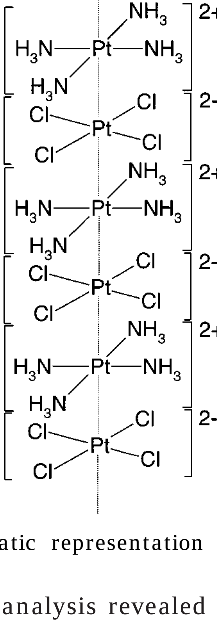

Figure 1. Schematic representation of the structure of Magnus' green salt.

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alternately stacked square planar $[\mathrm{Pt(NH_3)_4}]^{2+}$ and $[\mathrm{PtCl_4}]^{2-}$ moieties.[15-17] The green color of this Magnus' salt is very uncommon for platinum(II) compounds and arises as a consequence of the relatively short Pt−Pt distances in the quasi-one-dimensional structure.[12,15,18-20] These features also are the origin of the semiconducting properties of Magnus' green salt.[21-30] Unfortunately, Magnus' green salt and its isostructural derivative $[\mathrm{Pt(NH_2CH_3)_4}][\mathrm{PtCl_4}]$[12,13,31,32] are largely insoluble in water or common organic solvents, which severely restricts characterization and processing of such materials into useful objects.

Only recently, it has been found that increased solubility and associated processibility can be achieved by introduction of flexible side groups to the rigid metallic backbone.[33,34] These complexes of the type $[\mathrm{Pt(NH_2R)_4}][\mathrm{PtCl_4}]$ with R ranging from heptyl to tetradecyl are, however, pink and electrically insulating as a result of an increased Pt−Pt spacing.[33] Indeed, it has been stated earlier that pink compounds with intermetallic distances well above those in Magnus' green salt will always be obtained when R is an alkyl group containing more than one carbon atom, because of steric hindrance.[20] In the following, we demonstrate that this view is not correct and present the synthesis and materials properties of a soluble, semiconducting green derivative with R = (*S*)-3,7-dimethyloctane.

Experimental Section

Chemical Substances. $\mathrm{K_2[PtCl_4]}$ was obtained from Johnson Matthew, Zürich (Switzerland); the other substances (including solvents) were purchased from Fluka, Buchs (Switzerland), or Aldrich, Buchs (Switzerland) and used as received. Magnus' green salt and tetrakis(1-aminooctane)platinum(II) tetrachloroplatinate(II) were prepared according to the literature.[33]

Characterization. The elemental contents of carbon, hydrogen, nitrogen, and chlorine were analyzed by the microelemental service of the Laboratorium für Organische Chemie of ETH Zürich. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) was performed with equipment from Netzsch (TG 209 and DSC 200, respectively) under nitrogen atmosphere at heating rates of 10 °C/min if not otherwise indicated. IR spectra were taken with CsCl pellets on a Bruker IFS 66v spectrometer, UV/VIS spectra were taken on a Perkin-Elmer Lambda 900 spectrophotometer, and X-ray diffraction (XRD) patterns were taken on a Siemens D 5000 using Cu Kα radiation of 154 pm wavelength. For optical microscopy, a Leica DMRX microscope equipped with two polarizers and a Mettler Toledo FP82 HT hot stage was used. GC−MS measurements were performed on a Shimadzu GC/MS-QP5000, and the related masses are given in g/mol. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature on a Varian Gemini 300 or a Varian Mercury 400 MHz spectrometer. Chemical shifts in NMR spectra are given in ppm (δ) relative to tetramethylsilane. Abbreviations used for the description of the spectra are s = singlet, d = doublet, t = triplet, q = quartet, and br = broad. For the determination of the electrical resistance, pressed pellets of 10 mm diameter and 2 mm thickness were enclosed in a Teflon cylinder equipped with electrodes contacting both sides of the pellets. The temperature of measurement system was varied by immersing the Teflon cylinder in a hot sand bath or by placing the cylinder in a Dewar vessel filled with ice or dry ice−solvent mixtures. The temperature was measured within the Teflon cylinder at a distance of 1.5 mm from one of the electric contacts. The electrical resistance was determined with a Keithely 237 source measure unit after a constant temperature was established.

Synthesis of (*S*)-1-Amino-3,7-dimethyloctane. A total of 5 g (32.4 mmol) of (*S*)-citronellal and 2.54 g of (36.0 mmol) hydroxylamine hydrochloride were mixed in 50 mL of water and stirred for 30 min. Sodium carbonate (2.04 g, 19.2 mmol) in 30 mL of water was added dropwise, and the resulting mixture was stirred for 1 h. After extraction with diethyl ether, drying with $\mathrm{MgSO_4}$, and evaporation in vacuo, 4.9 g (89%) of (*S*)-3,7-dimethyloct-6-enal oxime were obtained as a colorless oil in a 1:1 ratio of isomers. ^{1}H NMR: isomer I: δ 0.96 (t, 3H, $\mathrm{CHC}H_3$, J = 6.6 Hz), 1.4 (m, 2H, CH), 1.61 (s, 3H, $=\mathrm{CC}H_3$), 1.69 (s, 3H, $=\mathrm{CC}H_3$), 1.7 (m, 1H, CH), 2.0 (m, 2H, CH), 2.3 (m, 2H, $\mathrm{C}H_2\mathrm{CH{=}N}$), 5.1 (m, 1H, C$H$=C), 7.43 (t, 1H, C$H$=COH, J = 6.6 Hz), 9.1 (s, br, 1H, CH=COH); isomer II: 0.96 (t, 3H, $\mathrm{CHC}H_3$, J = 6.6 Hz), 1.4 (m, 2H, CH), 1.61 (s, 3H, $=\mathrm{CC}H_3$), 1.69 (s, 3H, $=\mathrm{CC}H_3$), 1.7 (m, 1H, CH), 2.0 (m, 2H, CH), 2.3 (m, 2H, $\mathrm{C}H_2\mathrm{CH{=}N}$), 5.1 (m, 1H, C$H$=C), 6.75 (t, 1H, C$H$=COH, J = 5.4 Hz), 8.9 (s, br, 1H, CH=COH). GC-MS: $\mathrm{C_{10}H_{19}NO}$ (MW 169.26 g/mol), two peaks: 169 $[\mathrm{M}]^+$ and 154 $[\mathrm{M-CH_3}]^+$.

(*S*)-3,7-Dimethyloct-6-enal oxime (4 g, 23.6 mmol) was catalytically hydrogenated in 15 mL of ethanol in the presence of Pd/C (10%, 0.3 g) using a Parr apparatus. When no more $\mathrm{H_2}$ was consumed, the catalyst was filtered and the filtrate was evaporated in vacuo yielding (*S*)-3,7-dimethyloctanal oxime in quantitative yield as a 1:1 ratio of isomers. ^{1}H NMR: isomer I: 0.87 (d, 6H, $\mathrm{C(C}H_3)_2$, J = 6.6 Hz), 0.88 (d, 3H, $\mathrm{CHC}H_3$, J = 6.6 Hz), 1.2 (m, 4H, CH), 1.6 (m, 4H, CH), 2.3 (m, 2H, $\mathrm{C}H_2\mathrm{CH{=}N}$), 7.43 (t, 1H, C$H$=COH, J = 6.6 Hz), 8.8 (s, br, 2H CH=COH); isomer II: 0.87 (d, 6H, $\mathrm{C(C}H_3)_2$, J = 6.6 Hz), 0.88 (d, 3H, $\mathrm{CHC}H_3$, J = 6.6 Hz), 1.2 (m, 4H, CH), 1.6 (m, 4H, CH), 2.3 (m, 2H, $\mathrm{C}H_2\mathrm{CH{=}N}$), 6.75 (t, 1H, C$H$=COH, J = 5.4 Hz). ^{13}C NMR: (two isomers) 19.85, 20.13, 22.87, 22.96, 24.98, 25.03, 28.22, 31.24, 31.79, 32.43, 36.80, 37.13, 27.35, 37.44, 39.30, 39.40, 39.43, 151.61, 152.05. GC−MS: $\mathrm{C_{10}H_{21}NO}$ (171.28 g/mol), two peaks: 171 $[\mathrm{M}]^+$ and 156 $[\mathrm{M-CH_3}]^+$.

A solution of 2.0 g (12.8 mmol) of (*S*)-3,7-dimethyloctanal oxime in 40 mL of anhydrous diethyl ether was added to a stirred suspension of 0.97 g (25.5 mmol) of lithium aluminum hydride in 20 mL of diethyl ether. The mixture was heated under reflux for 18 h. After the mixture was cooled to room temperature, the reaction mixture was treated first with humid diethyl ether and then with water. The diethyl ether

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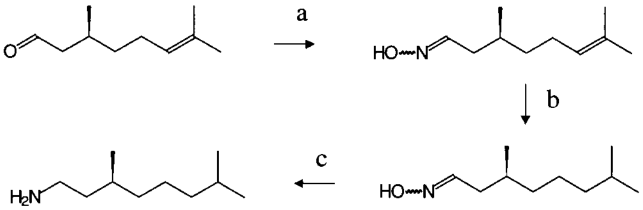
Scheme 1. Reaction Steps for the Synthesis of (*S*)-1-amino-3,7-dimethyloctane



a) NH_2OH/Na_2CO_3 b) $Pd/C/H_2$ c) $LiAlH_4$

layer was decanted, dried, and evaporated in vacuo. After distillation (0.66 mbar, 40 °C), 1.05 g (52%) of (*S*)-1-amino-3,7-dimethyloctane was obtained as a colorless oil. ^{1}H NMR: 0.87 (d, 6H, C(CH_3)$_2$, J = 6.6 Hz), 0.88 (d, 3H, CHCH_3, J = 6.6 Hz), 1.1 (m, 2H, CH), 1.3 (m, 4H, CH_2), 1.5 (m, 2H, CH_2-CH_2NH_2), 2.7 (m, 2H, C$H_2$$NH_2$).^{13}C NMR: 19.74, 22.66, 22.76, 24.78, 28.03, 30.57, 37.44, 39.36, 40.20, 41.36. GC-MS: $C_{10}H_{23}N$ (MW 157.29 g/mol), single peak: 157 $[M]^+$ and 142 $[M - CH_3]^+$.

Synthesis of Tetrakis((*S*)-1-amino-3,7-dimethyloctane)-platinum(II) Tetrachloroplatinate(II). A total of 1 g (2.42 mmol) of $K_2[PtCl_4]$ was heated in 20 mL of water under stirring at 60 °C. To this solution, 1.5 mL (9.68 mmol) of (*S*)-1-amino-3,7-dimethyloctane were added, and the reaction mixture was stirred at 60 °C. A green precipitate that formed after ca. 5 min dissolved after ca. 30 min. After 1 h, the reaction mixture, which consisted of a yellow organic phase and a clear aqueous phase, was allowed to cool to room temperature. Thereafter, 1 g (2.42 mmol) of $K_2[PtCl_4]$ in 10 mL of water was added. After ca. 30 min, a green product began to form. 50 mL toluene were mixed into the suspension and the green precipitate completely dissolved after heating to 70 °C. The solution was removed from the heating bath, and 100 mL of hexane were added, whereupon a green product precipitated again. The mixture was filtered through a Teflon filter (pore diameter 1 μm), and the remaining solids were washed with 30 mL hexane and dried at 10^{-2} mbar for 24 h. A yield of 63% was obtained. The elemental analysis revealed the following contents (in % w/w, calculated values in parentheses): C, 41.56% (41.52); H, 7.77 (7.67); N, 4.64 (4.84); Cl, 12.50 (12.26). Additional analytical data are discussed in the text below.

Results and Discussion

Synthesis of $[Pt(NH_2dmoc_4)][PtCl_4]$. The synthesis of the ligand (*S*)-1-amino-3,7-dimethyloctane (dmoc) was started from (*S*)-citronellal which was first converted to the (*S*)-3,7-dimethyloct-6-enal oxime with hydroxylamine hydrochloride (Scheme 1). It appeared not to be trivial to reduce the double bond and the oxime functionality of this intermediate in one step with lithium aluminum hydride. Therefore, the oxime derivative was first catalytically hydrogenated in the presence of Pd/C and subsequently reduced with lithium aluminum hydride to yield the desired amine; the latter was converted with $K_2[PtCl_4]$ to yield $[Pt(NH_2dmoc)_4]Cl_2$. Finally, $[Pt(NH_2dmoc)_4][PtCl_4]$ was obtained as a pure compound (cf. elemental analysis in the Experimental Section) by reaction of $K_2[PtCl_4]$ and $[Pt(NH_2dmoc)_4]Cl_2$.

Solid State Properties of $[Pt(NH_2dmoc)_4][PtCl_4]$. Remarkably, $[Pt(NH_2dmoc)_4][PtCl_4]$ exhibited the unusual color of Magnus' green salt. This finding is in contrast to the expectations in the literature[20] and to the pink color of the previously reported Magnus' salt derivatives with alkyl chains containing more than one carbon atom.[33] The UV/vis spectrum (Figure 2) of solid $[Pt(NH_2dmoc)_4][PtCl_4]$ deposited on quartz glass from toluene solution showed a pronounced absorption maximum (λ_{max}) at a wavelength of 310 nm. For comparison, a UV peak at 290 nm has been reported for the green $[Pt(NH_2R)_4][PtCl_4]$ compounds with R = H or methyl,[18] whereas the pink complexes with R = ethyl or octyl absorb at 251 and 255 nm (the latter in solution), respectively.[18,33] It appears that a band around 300 nm occurs only if the Pt−Pt distances are short enough to allow intermetallic interactions between the coordination units, and accordingly, this band was attributed to a transition of the d_{z^2} orbital of the $[PtCl_4]^{2-}$ to the p_z orbital of the $[Pt(NH_2R)_4]^{2+}$ unit.[13] A smaller, broad peak in $[Pt(NH_2dmoc)_4][PtCl_4]$ around 450 nm was assigned to d−d transitions.[19]

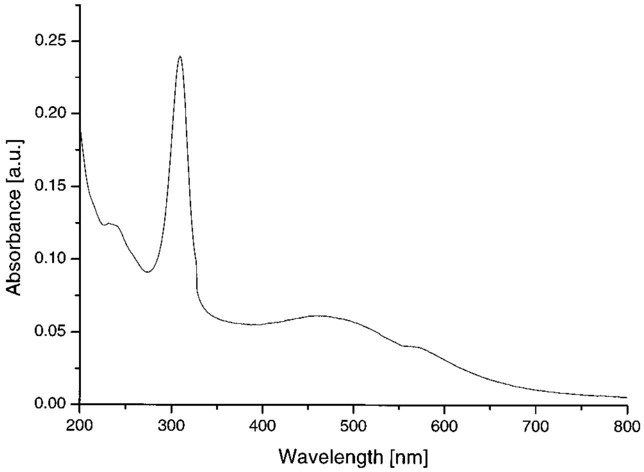


Figure 2. UV/VIS spectrum of a $[Pt(NH_2dmoc)_4][PtCl_4]$ film deposited from solution on quartz glass.

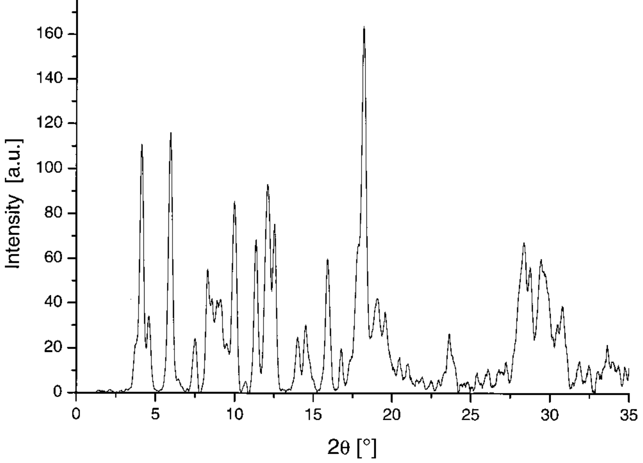


Figure 3. Wide-angle X-ray diffraction pattern of $[Pt(NH_2dmoc)_4][PtCl_4]$.

$[Pt(NH_2dmoc)_4][PtCl_4]$ was birefringeant when observed under crossed polarizers, indicating the crystalline nature of the solid, which was confirmed by powder X-ray diffraction (Figure 3). In contrast to the simple diffraction pattern of $[Pt(NH_2oc)_4][PtCl_4]$ (oc = octyl) which is consistent with a sheetlike arrangement of platinum arrays,[33] the pattern of $[Pt(NH_2dmoc)_4][PtCl_4]$ was more complex. The unit cell which could be best fitted to this diffraction pattern and complementary selected area electron diffraction results is monoclinic (space group P2/1) with the parameters a = 23.4 Å, b =

Table 1. IR Frequencies (in cm^{-1}) of Magnus' Green Salt and Related Compounds; oc = octyl, dmoc = (*S*)-3,7-dimethyloctyl

compound	ν(N−H)	ν(C−H)	δ(NH$_2$)	δ(CH$_2$) δ(CH$_3$)	γ(CH$_2$)	ν(Pt−N)	ν(Pt−Cl)
$[Pt(NH_3)_4][PtCl_4]$	3274		1631		829	500	311
	3135		1580				
$[Pt(NH_2dmoc)_4][PtCl_4]$	3236	2956	1569	1467	726.9	625	303
	3193	2926	1597	1383			
		2868		1366			
$[Pt(NH_2oc)_4][PtCl_4]$	3210	2957	1588	1467	723	605	319
	3132	2923		1378			
		2853					
$K_2[PtCl_4]$							323

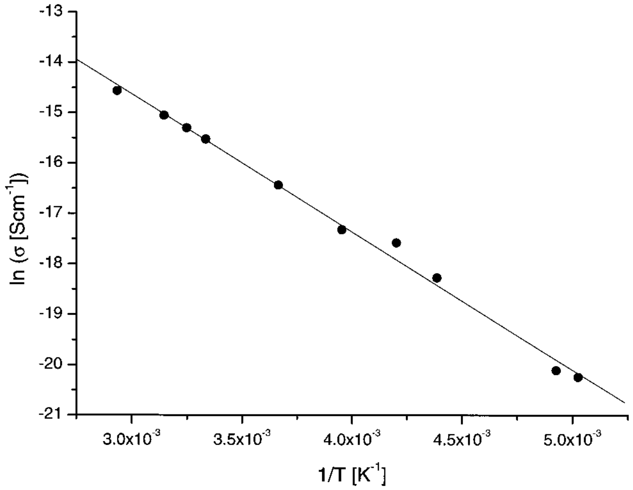


Figure 4. Plot of the logarithm of the conductivity (σ) of $[Pt(NH_2dmoc)_4][PtCl_4]$ as a function of the inverse temperature (T).

20.7 Å, c = 6.2 Å, and γ = 92°. Here, the c axis represents the monoclinic axis and the orientation axis of the platinum arrays. The resulting Pt−Pt distance corresponds to c/2, i.e., 3.1 Å.

Table 1 contains infrared (IR) frequencies of $[Pt(NH_2dmoc)_4][PtCl_4]$ and, for comparison, of Magnus' green salt and $[Pt(NH_2oc)_4][PtCl_4]$, where oc is octyl. The signals associated with the amine and alkyl groups were clearly visible and appeared in the expected regions. The Pt−N stretching vibrations were weak in all compounds, and ν(Pt−N) of $[Pt(NH_2dmoc)_4][PtCl_4]$ (625 cm^{-1}) was shifted by 20 cm^{-1} to higher frequencies compared to that of $[Pt(NH_2oc)_4][PtCl_4]$ (605 cm^{-1}). The Pt−Cl stretching vibration of $[Pt(NH_2dmoc)_4][PtCl_4]$ appeared at 303 cm^{-1}, which is exceptionally low compared to the frequencies of unperturbed vibrations in tetrachloroplatinates(II) (close to 320 cm^{-1}).[33] Such differences appear to indicate proximity between adjacent coordination units.[19] Therefore, besides color and UV spectra, IR spectra also indicate that the Pt−Pt distance in $[Pt(NH_2dmoc)_4][PtCl_4]$ is shorter than in $[Pt(NH_2oc)_4][PtCl_4]$ where the Pt−Cl stretching vibration (319 cm^{-1}) is in the common range of tetrachloroplatinate(II). For comparison, ν(Pt−Cl) in Magnus' green salt (311 cm^{-1}) also arises outside of the common range of tetrachloroplatinate(II).[33]

The thermal behavior of $[Pt(NH_2dmoc)_4][PtCl_4]$ was studied with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). As previously reported for $[Pt(NH_2oc)_4][PtCl_4]$,[33] the TGA and DSC thermograms of $[Pt(NH_2dmoc)_4][PtCl_4]$ similarly depended strongly on the heating rate. The results below refer to experiments carried out at a heating rate of 10 °C if not otherwise stated. In the temperature range between −80 and +200 °C, the DSC thermogram showed an irreversible transition upon heating at 163 °C which was due to simultaneous melting and decomposition as evident from optical microscopy. This decomposition temperature decreased linearly with the heating rate in the range of 1−10 °C/min, and extrapolation to a heating rate of 0 °C/min resulted in a decomposition temperature of 134 °C. Mass loss in thermogravimetric analysis began at ca. 180 °C. The residual mass remained constant at 40.0% of the original mass at temperatures exceeding 230 °C. This is above the initially present platinum content of 33.7%, as also observed in other complexes of the type $[Pt(NH_2R)_4][PtCl_4]$ and is probably due to the formation of platinum compounds instead of metallic platinum.[33]

The DC resistance of $[Pt(NH_2dmoc)][PtCl_4]$ was measured with two contacts clamped on each side of pressed pellets of 2 mm thickness and 10 mm diameter. An electrical resistance of 1 MΩ was found at room temperature, resulting in a conductivity of 1.6×10^{-7} S/cm. The same resistance was obtained from impedance measurements in the frequency range of 1−100 MHz. The independency of the resistance on the frequency agrees with the behavior of a band type semiconductor where the charge carriers are relatively mobile in the applied field.[22,35] The electrical conductivity followed the expression[27]

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

where σ is the electrical conductivity, σ_0 is an arbitrary constant, E_a is the activation energy, k_B is Boltzmann's constant, and T is the temperature (in K). Such dependence of the conductivity on the temperature is characteristic for semiconductors with a single thermally activated conduction process in the observed temperature interval,[22] and accordingly, 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 for $[Pt(NH_2dmoc)_4][PtCl_4]$, which is in the range of the values reported for Magnus' green salt (0.1−0.4 eV).[22−24,26]

The differences in Pt−Pt distances appear to be closely related to the electrical conductivity of the various Magnus' salt derivatives. Although the conduc-

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tivity of $[Pt(NH_2oc)_4][PtCl_4]$ was earlier reported[33] to be below 10^{-10} S/cm, for $[Pt(NH_2dmoc)_4][PtCl_4]$ and Magnus' green salt, values of respectively 1.6×10^{-7} and 1.5×10^{-6} S/cm were found in pressed samples in this work. The latter value agrees with that previously published for single crystals of Magnus' green salt.[21] Higher values up to 10^{-2} S/cm were also found for Magnus' green salt,[22,24,26,35] but those appear to originate in the presence of impurities.[23−25,35]

As obvious from the Introduction, the interplatinum distance in $[Pt(NH_2dmoc)_4][PtCl_4]$ is much shorter than in the corresponding compounds with linear 1-aminoalkanes[30] which is also reflected in the different colors (green vs pink) and conductivities (semiconducting vs insulating) of these substances. The interplatinum distances have been thought to be determined by the balance between the electrostatic attraction of the oppositely charged ions and steric effects,[16,33] and it has been suggested that the increase in the Pt−Pt distance in the pink compounds with the linear 1-aminoalkanes is due to steric hindrance.[20] However, it has been realized later from the X-ray single crystal structure determination of $[Pt(NH_2CH_2CH_3)_4][PtCl_4]$ that the increase in the Pt−Pt distance in the pink 1-aminoalkane derivatives is caused by an inclination of the coordination planes relative to each other; that is, the $[Pt(NH_2CH_2CH_3)_4]^{2+}$ and the $[PtCl_4]^{2-}$ units in the quasi-one-dimensional structure are not parallel in this case.[32] It has therefore been concluded that the efficiency of the crystal packing is responsible for the differences in the Pt−Pt distance. An alkane such as dmoc with two branching sites should render a dense packing of the alkyl groups more difficult, and hence, the influence of the crystal packing could become less important; that is, the influence of the electrostatic attraction between the oppositely charged coordination units could become more important and lead to a decrease in the Pt−Pt distances. For comparison, we have described recently[36] a 1-amino-2-ethylhexyl (NH_2-eh) derivative of the Magnus' salt type. The alkane group in this compound has one branching site and is therefore considered to be less regular than a linear alkane but more regular than a dmoc group. Although the Pt−Pt distances could not be quantified in the NH_2-eh derivative, it appeared from the color and the electrical conductivity (10^{-9}−10^{-10} S/cm) that the interplatinum distances were indeed shorter than in the compounds with the linear 1-aminoalkanes although still larger than in Magnus' green salt and the NH_2-dmoc derivative, respectively.

Solutions. $[Pt(NH_2dmoc)_4][PtCl_4]$ was insoluble in cold and hot acetone, water, or methanol. The platinum complex dissolved, however, in tetrahydrofuran (THF) and dimethyl formamide (DMF) but decomposed within a few hours as indicated by a color change from green to yellow. Stable green solutions of $[Pt(NH_2dmoc)_4][PtCl_4]$ could be obtained in toluene, *p*-dichlorobenzene, or xylene at 80 °C or in chloroform or dichloromethane at their respective boiling temperatures. After evaporation of the solvents, $[Pt(NH_2dmoc)_4][PtCl_4]$ was recovered; that is, the complex did not decompose in those solvents under the applied conditions. Excellent solubility was found in toluene and xylene; dissolution proceeded slowly at room temperature, whereas at 80 °C dissolution was complete within a few minutes. When the toluene or xylene solutions containing up to 5% w/w of the complex were cooled to room temperature, they remained homogeneous for a few hours, but then $[Pt(NH_2dmoc)_4][PtCl_4]$ slowly precipitated. In chloroform, *p*-dichlorobenzene and dichloromethane precipitation was relatively fast upon cooling from the respective boiling temperatures to room temperature. Freshly prepared solutions in toluene did not show birefringeance up to concentrations of 20% w/w of $[Pt(NH_2dmoc)_4][PtCl_4]$. Cooling from 80 °C to − 78 °C did not induce any visible changes in solutions observed in a microscope for samples in concentrations of 0.1−1% w/w. In the composition range of 2−5% w/w of the complex, the solutions separated in a solvent and a gellike phase upon cooling from 80 °C to room temperature. A homogeneous solution was obtained again when the samples were heated to 80 °C. At concentrations of 5−50% w/w of the complex, a single, solidlike phase appeared upon cooling to −78 °C. Upon heating to 80 °C, a viscous solution formed, which again solidified upon cooling to −78 °C. Observations in the polarizing microscope revealed that gelation/crystallization started around −8 °C at concentrations of 10−50% w/w and at around −28 °C at concentrations of 1−5% w/w of the complex (cooling rate of 10 °C/min). At the

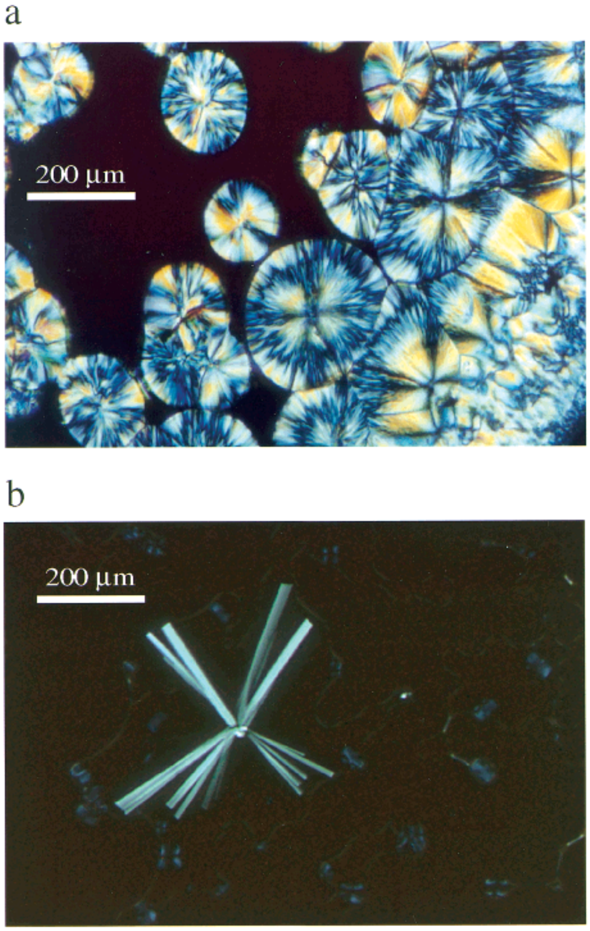

Figure 5. Polarized optical microscope images of a crystallized $[Pt(NH_2dmoc)_4][PtCl_4]$ film. (a) Spherulithic structures upon quenching of a 10% w/w $[Pt(NH_2dmoc)_4][PtCl_4]$ solution from 80 °C to room temperature and (b) hedritic crystals formed after slow crystallization from solution.

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(36) Bremi, J.; Caseri, W.; Smith, P. *J. Mater. Chem.* **2001**, *11*, 2593.

respective temperatures, birefringeance appeared when the samples were placed between crossed polarizers, indicating the formation of an increased order in the samples. As shown in the optical micrograph in Figure 5a, spherulitic structures developed when a film of a 5 or 10% w/w $[Pt(NH_2dmoc)_4][PtCl_4]$ solution was quenched from 80 °C to room temperature. After several days, the presence of hedritic crystals was also observed (Figure 5b).

The number average molecular weight (M_n) of $[Pt(NH_2$-$dmoc)_4][PtCl_4]$ was determined by vapor phase osmometry in toluene in the concentration range of 0.1−1.15% w/w at 70 °C. As noted above, at lower temperatures, $[Pt(NH_2dmoc)_4][PtCl_4]$ slowly precipitated. A value for M_n of 9×10^3 g/mol was found, which corresponds to an average array of about 16 platinum atoms.

^1H NMR spectra in d^8-toluene yielded little information. Broad signals with unresolved couplings of the alkyl groups of the dmoc ligands appeared between 0.9 and 1.8 ppm; a very broad signal at 3.6 ppm was attributed to the CH_2NH_2 fragments. This peak was shifted by 0.9 ppm to lower field compared to free dmoc as a result of the electron withdrawing effect of the Pt^{2+} ions.

Conclusions

Compounds of the formula $[Pt(NH_2R)_4][PtCl_4]$, where R denotes a hydrogen atom or an alkyl group, can be divided into pink and green compounds.[33] The Pt−Pt distances in the green compounds are considerably shorter than in the pink substances.[20] Indeed, it appears that the green color arises as a consequence of Pt−Pt interactions[20] and that this color is characteristic only for complexes with Pt−Pt distances below 3.4 Å.[12] So far, such compounds have been obtained only with R = H or methyl, respectively, where the Pt−Pt spacing is around 3.25 Å (compared to 3.1 Å estimated for the complex prepared in this work). It has been suggested that the stacking of the coordination units in compounds of the type $[Pt(NH_2R)_4][PtCl_4]$ is strongly influenced by electrostatic interactions between the oppositely charged coordination units and, additionally, repulsive steric effects,[16,33] and it has been concluded that substituents of more than one carbon atom cause an expansion of the Pt−Pt spacings because of steric hindrance, resulting in pink compounds.[20] We have, however, demonstrated here that this concept is not generally true because the present $[Pt(NH_2dmoc)_4][PtCl_4]$ exhibits a green color, and the related compound with linear alkyl groups, $[Pt(NH_2oc)][PtCl_4]$, is pink. We conclude, therefore, that the packing of the alkyl groups and not steric hindrance per se dictates the Pt−Pt distances in the solid state. On the basis of this finding, it cannot be excluded that substituted amines might be found which allow the formation of even shorter Pt−Pt spacings than in Magnus' green salt, ideally down to the length of Pt−Pt bonds (typically 2.6−2.8 Å),[33] which would be of major interest in regard to the electrical conductivity of such compounds.

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