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A new compound derived from Magnus' green salt: solid state structure and evidence for platinum chains in solution

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The complex $[Pt(NH_2Eh)_4][PtCl_4]$, where Eh = 2-ethylhexyl, was synthesized and analyzed using various methods. The results imply that $[Pt(NH_2Eh)_4][PtCl_4]$ forms supramolecular structures composed of chains of platinum atoms not only in the solid state but, most remarkably, also in solution, as indicated by membrane osmometry and viscosimetry. At 37 °C in toluene, the chains are present in a worm-like structure and contain *ca.* 750 platinum atoms on average. The solid state properties of $[Pt(NH_2Eh)_4][PtCl_4]$ are distinct from those of related compounds with linear 1-aminoalkanes. In particular, $[Pt(NH_2Eh)_4][PtCl_4]$ is cryochromic and amorphous. The 2-ethylhexyl chains obviously prevent side chain crystallization and, as a consequence, electrostatic interactions between the $[Pt(NH_2Eh)_4]^{2+}$ and $[PtCl_4]^{2-}$ units seem to dominate the structure formation of $[Pt(NH_2Eh)_4][PtCl_4]$.

Introduction

A number of platinum compounds form solid state structures with linearly arranged platinum atoms.[1–3] The most prominent of these structures is $[Pt(NH_3)_4][PtCl_4]$ (Magnus' green salt, Fig. 1) which contains linear chains of platinum atoms separated by 3.23–3.25 Å,[4–6] a distance which is large compared to typical Pt–Pt bond lengths (2.6–2.8 Å).[7] Hence, the linear arrangement of the platinum atoms is determined by electrostatic interactions between the $[Pt(NH_3)_4]^{2+}$ and $[PtCl_4]^{2-}$ moieties rather than metal–metal bonds,[8,9] although Pt–Pt interactions still exist.[8] These interactions are considered to cause the unusual color of Magnus' green salt.[4,8,10,11] Complexes of the type $[Pt(NH_2R)_4][PtCl_4]$, where R is an alkyl group, have also been described. The compound with R = methyl shows the same color and structure as Magnus' green salt (Pt–Pt distance 3.25–3.29 Å[4,5]), while the compounds with R = ethyl, propyl, or butyl are pink (or red).[7] From the various pink complexes, only the structure of the 1-aminoethane compound has been resolved by X-ray diffraction, revealing linearly arranged platinum atoms separated by 3.62 Å,[12] and it has been suggested, but not shown, that the packing of alkyl groups with two or more carbon atoms extends the Pt–Pt distance compared to that in the green complexes.[13]

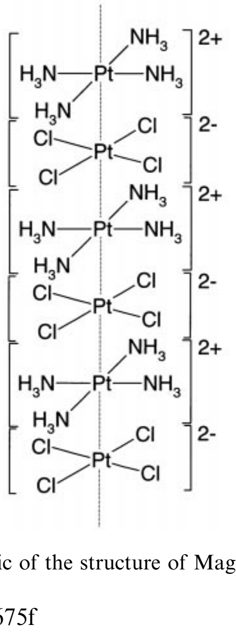

Fig. 1 Schematic of the structure of Magnus' green salt.

The above-mentioned compounds are largely insoluble in water and common organic solvents without decomposition and, hence, there is no evidence for supramolecular structures in solution. Recently, compounds of the composition $[Pt(NH_2R)_4][PtCl_4]$, with R ranging from heptyl to tetradecyl, have been shown to be soluble at elevated temperatures (typically 50–110 °C) in organic solvents.[7,14] Upon cooling to room temperature, they readily form thermoreversible gels consisting of fibrillar structures. Most likely, crystallization of the alkyl side chains is the dominant factor in the reversible formation of these gels. It is not known whether the chain structure in any of the above-mentioned complexes is preserved in solution, or if the linear arrangement of the platinum atoms is simply a consequence of the crystal packing. In this work, we attempt to address this particular aspect by suppressing side chain crystallization by employing a branched ligand, *i.e.* 1-amino-2-ethylhexane (NH_2Eh).

Results and discussion

Solutions

$[Pt(NH_2Eh)_4][PtCl_4]$ was found to be highly soluble in various organic solvents. Dissolution proceeded slowly at room temperature, a property which is characteristic for high molecular weight polymers. At 60 °C, it took *ca.* 1 h to dissolve $[Pt(NH_2Eh)_4][PtCl_4]$ in tetrahydrofuran, chloroform, benzene, toluene or xylene. No dissolution was observed in water, acetone, ethanol, dichloromethane or hexane. In the following experiments, $[Pt(NH_2Eh)_4][PtCl_4]$ was always dissolved at 60 °C prior to adjusting the temperature to the indicated value. At room temperature, the birefringence observed in the solid state (*vide infra*) was lost in solution at concentrations of the complex in toluene up to about 40% w/w. In marked contrast to the compounds with linear alkyl chains,[7,14] $[Pt(NH_2Eh)_4][PtCl_4]$ did not form gels upon cooling hot solutions to room temperature. ^1H and ^{13}C NMR spectra of

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$[Pt(NH_2Eh)_4][PtCl_4]$ (5% w/v in $CDCl_3$) showed the expected peaks which were, however, too broad to resolve any ^3J(H,H) couplings in the ^{1}H NMR spectra.

The UV/VIS spectrum of $[Pt(NH_2Eh)_4][PtCl_4]$ in tetrahydrofuran in the range 250–800 nm was dominated by an absorption maximum (λ_{max}) at 263 nm (extinction coefficient $\varepsilon = 32000\ M^{-1}\ cm^{-1}$, accompanied by a shoulder around 290 nm. These bands did not appear in $[Pt(NH_2Eh)_4]Cl_2$, $K_2[PtCl_4]$ or free 1-amino-2-ethylhexane; it may, therefore, indicate an interaction between $[Pt(NH_2Eh)_4]^{2+}$ and the $[PtCl_4]^{2-}$ units.[4] Based on the detailed analysis of other complexes of the Magnus' salt type,[4,11] these absorptions can be attributed to interionic electron transfers from the d_{z^2} orbitals of the anions into the p_z orbitals of the cations. Absorption maxima at 327 and 390 nm arise in aqueous solutions of $K_2[PtCl_4]$. They are caused by d–d transitions and are expected to shift towards lower energies in compounds of the Magnus' salt type with metal–metal distances in the region 3.25–3.6 Å.[4] Indeed, $[Pt(NH_2Eh)_4][PtCl_4]$ exhibits a shoulder at 356 nm (on the side of the dominant signal at 263 nm) and an absorption maximum at 519 nm ($\varepsilon = 70\ M^{-1}\ cm^{-1}$). Hence, the UV/VIS spectra indicate significant Pt–Pt interactions when the complex is in solution.

In order to further investigate if the $[Pt(NH_2Eh)_4]^{2+}$ and the $[PtCl_4]^{2-}$ units formed supramolecular structures in solution, the molecular weight of the dissolved complex was determined by membrane osmometry in toluene at 37 °C (the lowest temperature available with our equipment). The concentration range suited for the measurements was 1–8 mg mL^{-1}, corresponding to *ca.* 1–8 mM or 0.1–0.9% w/w. The measurements were within 6% in this concentration range and yielded a number average molecular weight (M_n) of 4×10^5 g mol^{-1}, which corresponds to a supramolecular assembly with *ca.* 750 platinum atoms. At 60 °C, the values were less reproducible, perhaps due to dynamic processes such as reversible ligand dissociation, but it was confirmed that M_n was still high (roughly 2.5×10^5 g mol^{-1}). For comparison, M_n values for $[Pt(NH_2R)_4][PtCl_4]$ (R = tetradecyl) were also measured at 60 °C (measurements markedly below this temperature could not be performed due to gel formation[7]). For this complex, the molecular weights were too low to be determined accurately (the level of detection corresponded to a chain of *ca.* 15 Pt atoms).

To qualitatively confirm the existence of high molecular weight structures of $[Pt(NH_2Eh)_4]^{2+}$ and $[PtCl_4]^{2-}$ in toluene solution at 37 °C, the specific viscosity (η_s) was measured by capillary viscosimetry of solutions containing 1.25 mg mL^{-1} of the complex (the highest concentration that yielded reliable results with the available viscosimeters). The scatter of the η_s values was as high as 20%, which maybe caused by degradation of the supramolecular structures in the shear fields of the capillary; therefore, it was not possible to determine the intrinsic viscosity with a high precision. Nonetheless the η_s values around 0.9 mL g^{-1} demonstrate the high molecular weight nature of the dissolved product. For comparison, the η_s of atactic polystyrene with an M_n of 4.0×10^5 g mol^{-1} is 0.1 mL g^{-1} under the same conditions, *i.e.* clearly lower (of course, η_s depends not only on the molecular weight, but also on other factors, such as the hydrodynamic volume and the shape of the dissolved structures).

If the coordination planes in $[Pt(NH_2Eh)_4][PtCl_4]$ are perfectly coplanar, the dissolved structures are likely to behave as rigid rods in solution. For solutions of ideal $[Pt(NH_2Eh)_4][PtCl_4]$ rods with $M_n = 4 \times 10^5$ g mol^{-1} and a Pt–Pt distance of the order of 3.2–3.5 Å, lyotropic behavior is expected to set in at $[Pt(NH_2Eh)_4][PtCl_4]$ volume fractions around 0.05.[15] However, solutions containing 30% w/w of the complex did not display a liquid-crystalline phase. Thus, it is likely that the chain backbone is not rigid in solution but probably adopts a worm-like structure, probably due to non-coplanarity of the $[Pt(NH_2Eh)_4][PtCl_4]$ coordination planes.

Solid state

The color of the 1-amino-2-ethylhexyl compound in the solid state is dark violet (or greyish, probably depending on the surface roughness of the solids or differences in light reflection), and is similar to that of $[Pt(en)_2][PtCl_4]$ (en = 1,2-diaminoethane)[5,16] but different from that of Magnus' green salt and the hitherto described complexes of the type $[Pt(NH_2R)_4][PtCl_4]$, which are pink or green.[7] Upon cooling to *ca.* −55 °C, however, $[Pt(NH_2Eh)_4][PtCl_4]$ reversibly changed color to green. This behavior is in contrast to that of the pink compounds with the linear alkyl chains, which stay pink at least down to −196 °C (in liquid nitrogen). Since it has previously been concluded that the color of $[Pt(NH_2R)_4][PtCl_4]$ complexes is related to the Pt–Pt distance (see Introduction), we assume that the Pt–Pt spacing of $[Pt(NH_2Eh)_4][PtCl_4]$ is smaller than that in the pink compounds with the linear alkyl groups, but similar to that in $[Pt(en)_2][PtCl_4]$ (3.40 Å[5]). Hence, the color change at *ca.* −55 °C appears to indicate a decrease in the Pt–Pt distance, probably to a value that is of the same order as those observed in the green compounds (around 3.25 Å, see Introduction). The color transition at −55 °C was not associated with a significant energy change, as far as could be concluded from the DSC measurements reported below.

While the platinum atoms in complexes with heptyl or longer alkyl chains are arranged in well-resolved parallel sheets or hexagonal columns,[7] very limited order was observed for $[Pt(NH_2Eh)_4][PtCl_4]$. X-Ray diffraction (XRD) patterns comprised only extremely weak reflections at 7.7 and 12.9 Å. Obviously, the 2-ethylhexyl-substituted complex is largely amorphous, although some birefringence was observed when $[Pt(NH_2Eh)_4][PtCl_4]$ was placed between crossed polarizers in the optical microscope. After drying dilute toluene solutions (*ca.* 10 µg mL^{-1}) of $[Pt(NH_2Eh)_4][PtCl_4]$ by evaporation, thin structured features with diameters down to the resolution limit of the electron microscope assembled into cubic-like objects with typical dimensions around 200 nm, which themselves merged into larger aggregates (Fig. 2). Very rarely, arrays of parallel structures separated by 13–14 Å were found. Weak

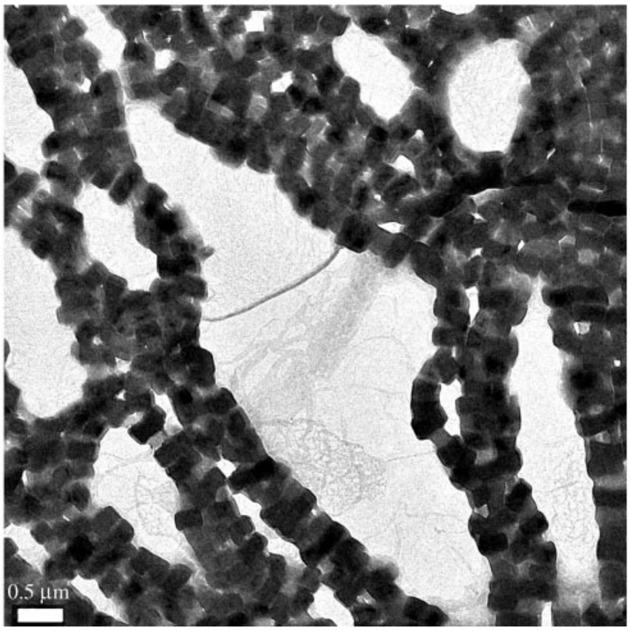

Fig. 2 Transmission electron micrograph of $[Pt(NH_2Eh)_4][PtCl_4]$ structures obtained after evaporation of the solvent from a 10 ppm solution of the complex in toluene.

Table 1 IR frequencies (in cm^{-1}) of bands observed for [Pt(NH$_2$R)$_4$][PtCl$_4$] {R = 2-ethylhexyl (Eh) or octyl (Oct)}

Compound	ν(N–H)	ν(C–H)	δ(NH$_2$)	δ(CH$_2$, CH$_3$)	γ(CH$_2$)	ν(Pt–N)	ν(Pt–Cl)
[Pt(NH$_2$Eh)$_4$][PtCl$_4$]	3241 3191 3137 3051	2958 2929 2872	1596 1569	1465 1379	734	619	306
[Pt(NH$_2$Oct)$_4$][PtCl$_4$]	3210 3133	2957 2924 2853	1586	1467 1378	724	605	319

reflections related to a distance of 13 Å were also observed with electron diffraction, corresponding to the weak features observed in the XRD patterns mentioned above. It appears that a small fraction of the [Pt(NH$_2$Eh)$_4$][PtCl$_4$] was able to form ordered structures comprised of linear arrays of platinum atoms, similar to the structures of the complexes with linear alkyl chains.[7]

Table 1 contains the IR frequencies of bands observed for [Pt(NH$_2$Eh)$_4$][PtCl$_4$] and, for comparison, [Pt(NH$_2$Oct)$_4$][PtCl$_4$] (Oct = octyl). The IR spectrum of [Pt(NH$_2$Eh)$_4$][PtCl$_4$] was not significantly affected upon cooling to temperatures where the compound adopted a green color. Most of the frequencies of [Pt(NH$_2$Eh)$_4$][PtCl$_4$] differ from those of [Pt(NH$_2$Oct)$_4$][PtCl$_4$]. In particular, ν(Pt–N) and ν(Pt–Cl) of [Pt(NH$_2$Eh)$_4$][PtCl$_4$] are shifted by 14 cm^{-1} to higher and 13 cm^{-1} to lower frequencies, respectively, compared to [Pt(NH$_2$Oct)$_4$][PtCl$_4$]. In a number of complexes with very weak or absent Pt–Pt interactions, such as [Pt(NH$_2$Oct)$_4$][PtCl$_4$], K$_2$[PtCl$_4$], and the pink Magnus' salt analogues, ν(Pt–Cl) of the tetrachloroplatinate(II) unit arises in the narrow range 319–323 cm^{-1}, whereas the corresponding value in Magnus' green salt with considerable Pt–Pt interactions, drops to 311 cm^{-1},[7] which is in the same region as ν(Pt–Cl) for the ethylhexyl-substituted complex. Since it has been reported[11] that ν(Pt–Cl) in tetrachloroplatinate(II) is influenced by Pt–Pt interactions, the ν(Pt–Cl) of [Pt(NH$_2$Eh)$_4$][PtCl$_4$] (306 cm^{-1}) indicates that the Pt–Pt distances are short enough to allow significant Pt–Pt interactions.

The thermal properties of [Pt(NH$_2$Eh)$_4$][PtCl$_4$] were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC thermograms did not show any transition between −80 and 210 °C at a heating rate of 10 °C min^{-1}; the onset of decomposition occurred at the latter temperature (at a heating rate of 1 °C min^{-1}, decomposition commenced at *ca.* 190 °C). Decomposition was also observed under the microscope at similar temperatures. Mass loss in TGA started at *ca.* 200 °C at a heating rate of 10 °C min^{-1} and at *ca.* 135 °C at 0.2 °C min^{-1}, and the corresponding maximum rates of weight loss appear at 266 and 192 °C min^{-1}, respectively. Extrapolated to a heating rate of 0 °C min^{-1}, maximum weight loss should arise at *ca.* 180 °C. At 600 °C, the remaining mass corresponds roughly to the mass of platinum initially present in [Pt(NH$_2$Eh)$_4$][PtCl$_4$].

Conclusions

In summary, we have demonstrated that 2-aminoethylhexyl chains in [Pt(NH$_2$Eh)$_4$][PtCl$_4$] suppress crystallization in compounds of the type [Pt(NH$_2$R)$_4$][PtCl$_4$]. The resulting solids are highly amorphous. The color of [Pt(NH$_2$Eh)$_4$][PtCl$_4$] turned from greyish-violet to green at *ca.* −55 °C, which appears to indicate a decrease in the Pt–Pt distance. As deduced from solution viscosity measurements, [Pt(NH$_2$Eh)$_4$][PtCl$_4$] assembled in supramolecular structures whose number average molecular weight was determined by membrane osmometry to be 4×10^5 g mol^{-1} at 37 °C.

Experimental section

General

K$_2$[PtCl$_4$] was obtained from Johnson Matthew & Brandenberger (Zürich, Switzerland) and other substances (including solvents) from Fluka and Aldrich (Buchs, Switzerland). Tetrakis(aminooctane)platinum(II) tetrachloroplatinate(II) was prepared according to procedures described in the literature.[7] Elemental analyses of carbon, hydrogen, nitrogen, and chlorine were performed by the microelemental service of the Laboratorium für Organische Chemie at ETH Zürich, and noble metal analyses by the analytical service of the Laboratorium für Anorganische Chemie at ETH Zürich. Thermogravimetric analysis and differential scanning calorimetry was performed with equipment from Netzsch (TG 209 and DSC 200, respectively) under a nitrogen atmosphere at heating rates of 10 °C min^{-1}, unless otherwise indicated. IR spectra were recorded from CsCl pellets on a Bruker IFS 66v spectrometer. For optical microscopy, a Leica DMRX polarizing microscope and a Mettler Toledo FP82 HT hot stage were used. X-Ray diffraction patterns were obtained on a Kiessig small-angle-scattering camera, equipped with a Seifert ISO-Debyeflex 2002 polaroid cassette, using Ni-filtered Cu-Kα radiation (wavelength 1.5416 Å). Membrane osmometry was carried out with a Knauer osmometer using a regenerated cellulose RC 52 (Schleicher & Schüll, Basel, Switzerland) membrane. Transmission electron microscopy was performed with a Philips CM12 electron microscope equipped with a precooled cold stage (MIDILAB) using a dry nitrogen counter-flow loading device. The samples were kept in the MIDILAB unit for 2 h at −80 °C at a pressure below 10^{-7} mbar, transferred to a specially designed Gatan cryoholder, and examined at an acceleration voltage of 100 kV below −175 °C. Images were recorded with a Gatan 694 slow scan CCD camera at a low electron flux (0.5 e Å^{-2}), to avoid reduction of the complex to elemental platinum.

Synthesis of tetrakis(1-amino-2-ethylhexane)platinum(II) tetrachloroplatinate(II)

K$_2$[PtCl$_4$] (2.2 g, 5.3 mmol) was heated in 40 mL water to 60 °C. To this solution, 17.5 mL (107 mmol) 1-amino-2-ethylhexane were added, and the reaction mixture stirred at 60 °C. A yellow precipitate formed after *ca.* 5 min, but dissolved after *ca.* 30 min. After 1 h, the reaction mixture, which consisted of a yellow organic phase and an opaque aqueous phase, was allowed to cool to room temperature. Thereafter, another 2.2 g (5.3 mmol) of K$_2$[PtCl$_4$] in 40 mL water were added. Immediately, a pink solid precipitated. Rapidly, 50 mL hexane were mixed into the suspension, and the pink precipitate completely dissolved. Upon addition of 30 mL ethanol, a pink product precipitated again. The mixture was filtered through a Teflon® filter (pore diameter 1 µm), and the remaining solids were washed in the funnel with *ca.* 10 mL hexane and then dried at 10^{-2} mbar for 24 h, whereupon the color of the product turned from pink to grey. The grey product was purified by dissolving it in 60 mL chloroform at

60 °C, cooling to room temperature and filtering through a Teflon® filter (pore diameter 1 µm). The filtrate was treated with 50 mL ethanol, and the precipitate was collected by filtration through a sintered glass funnel (N4), washed in the funnel with 50 mL ethanol, and dried at 10^{-2} mbar for 24 h. A yield of 88% (4.89 g) was obtained. Elemental analysis (in % w/w, calculated values in parentheses): C 36.55 (36.64), H 6.96 (7.30), N 5.31 (5.34), Cl 13.54 (13.52).

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