# Characterization of a New One-dimensional Conductor formed by Partial Oxidation of Magnus Green Salt

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The reaction of Magnus green salt $[Pt(NH_3)_4][PtCl_4]$ in $HClO_4$ (1 M) with various (chloro)(hydroxo)$Pt^{IV}$ complexes or with $H_2O_2$ gives a single phase partially oxidized conducting salt which contains directly interacting Pt atom chains (Pt–Pt 2.85 Å) adjacent to parallel chlorine bridged $Pt^{II}$–$Pt^{IV}$ chains.

The preparation of an oxidized product of Magnus green salt $[Pt^{II}(NH_3)_4][Pt^{II}Cl_4]$ (Mgs) has interested many researchers.[1-6]

We have succeeded in obtaining copper-coloured needles of a new partially oxidized Magnus green salt (poMgs) by treating

**Table 1.** Chemical analysis (samples dried at 30 °C/$10^{-3}$ Torr).

|  | %Pt | %Cl | %N | %O |
|---|---|---|---|---|
| Mean from 8 products (s.d.) | 53.07 (0.63) | 23.49 (0.65) | 8.89 (0.19) | 12.37 (1.00) |
| Recrystallized product | 53.25 | 23.33 | 9.04 | 11.19 |
| Calcd. for (1) ($x = 4$) | 53.16 | 23.46 | 8.72 | 12.46 |

solid Mgs, at room temperature, in an aqueous 1 M perchloric acid medium, with the following oxidizing agents: $[Pt^{IV}\text{-}(NH_3)_4XY](ClO_4)_2$ (X,Y = $Cl^-$, $OH^-$), $K_2[Pt^{IV}Cl_6]$, $M_2[Pt^{IV}Cl_4\text{-}(OH)_2]$ (M = $K^+$, $H^+$), and $H_2O_2$ [presumably via a (diaquo)$Pt^{IV}$ complex]. Some of the products were recrystallized from $HClO_4$ (1 M). Using X-ray powder diffraction measurements, obtained at room temperature, it was established that the copper-coloured solids are single phase materials having tetragonal symmetry with lattice parameters $a = 15.07$ and $c = 5.70$ Å, quite different from those of Mgs itself ($a_{Mgs} = 9.03$, $c_{Mgs} = 6.49$ Å [7]). The results of elemental analysis, listed in Table 1, indicate the overall chemical formula $PtN_{2\cdot33}Cl_{2\cdot44}O_{2\cdot84}H_{7\cdot95}$ (H content by difference). Our poMgs thus shows a N:Pt ratio exceeding that of Mgs. The mean oxidation state of platinum is 2.41($\pm$0.02) as determined by oxidative titration. In addition, the spectrophotometric determination[8] of the $ClO_4^-$ content gave 16($\pm$0.3) weight %.

Preliminary measurements of the d.c. electrical conductivity were made using pressed pellets of the poMgs. The room temperature conductivity $\sigma_{RT}$ is ca. $10^{-2}$ $\Omega^{-1}$ $cm^{-1}$. Between 273 and 70 K, the product behaves like a doped semiconductor [$\sigma = \sigma_0 \exp(-E_g/2k_BT)$] with $E_g$ ranging from 0.05—0.06 (sample saturated with $H_2O$ at 293 K) to 0.03—0.04 eV (sample outgassed at 293 K).

The Raman spectra of our copper-coloured product were recorded at room temperature with 616, 514.5, and 457.9 nm excitation lines, by spinning the powdered samples rapidly. Resonance enhancement was observed in the bands at 324, 648, 962, and 1275 $cm^{-1}$ corresponding to the $\nu_1$ (Cl–$Pt^{IV}$–Cl) fundamental symmetric stretching vibration and its associated 1st to 3rd overtones. It is interesting to note that the Raman spectra of our product are very similar to the spectrum of a yellow salt recently prepared in our laboratory.[9] This salt is presumably a Wolffram's type salt with an intrachain Pt–Pt distance of 5.56 Å and an analysis consistent with the formula $[Pt^{II}(NH_3)_4]_{0\cdot85}[Pt^{IV}(NH_3)_4Cl_2]_{0\cdot15}(ClO_4)_2$ (low $Pt^{IV}$:$Pt^{II}$ ratios have been reported in the case of Wolffram's red salt[10]). We have checked that recrystallization of our poMgs causes no modification in the Raman spectrum and that the presence of an impurity is not responsible for the resonance effect.

X-Ray photoelectron spectroscopy of our poMgs indicated that the Pt $4f_{7/2}$ and $4f_{5/2}$ peaks were shifted to higher binding energy by $+$ 0.9 eV from the corresponding peaks in Mgs. In addition, a shoulder at $+$ 1.5—2 eV from the maximum suggested that 15—20% of the platinum atoms are in the IV oxidation state, at least in the X.P.S. time-scale (ca. $10^{-16}$ s).[11] Although a satellite effect cannot be excluded,[11] it is nevertheless interesting to note that a similar doublet structure was found in the case of the one-dimensional conductor $K_2Pt(CN)_4Br_{0\cdot3}\cdot2.3H_2O$ at 153 K.[12,13]

The X-ray powder diffraction spectrum of the poMgs may be first-order indexed as tetragonal with $a' = 7.535$ and $c = 5.70$ Å. Such a lattice would be strikingly similar to that described by Schöllhorn,[4] which consists of partially oxidized Mgs type chains with a Pt–Pt distance of $c_s/2 = 2.86$ Å ($a_s = 7.475$, $c_s = 5.721$ Å; 2 Pt atoms in the unit cell). However, taking account of low intensity lines [<5% of the most intense (200) line] required doubling of the parameter in the direction perpendicular to the stacking $c$-axis, which gives for our poMgs a unit cell volume four times larger ($a = 2a' =$

15.07 Å). If the lattice consisted exclusively of chains with direct Pt–Pt contacts, the cell should contain eight of the chemical units $PtN_{2\cdot33}Cl_{2\cdot44}O_{2\cdot84}H_{7\cdot95}$ and its calculated density would be as high as 3.77 g $cm^{-3}$. However preliminary density measurements of our copper-like product gave a value between 3.23 and 3.33 g $cm^{-3}$ which means that the cell actually contains seven chemical units (calculated density = 3.30 g $cm^{-3}$).

All these results suggest to us the structural formula (1) for our poMgs which corresponds to the overall formula $PtN_{2\cdot29}$-$Cl_{2\cdot43}O_{2\cdot86}H_{8\cdot00}$ with $x = 4$. Thus there are in the lattice two

$$[Pt^{2\cdot33}(NH_3)_4Pt^{2\cdot33}Cl_4]_3[Pt^{II/IV}(NH_3)_4Cl](ClO_4)_4(H_2O)_x$$

**(1)**
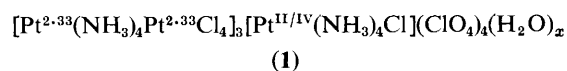
types of linear chains running parallel to the $c$ axis: (i) partially oxidized Mgs type chains $\cdots$ $[Pt^{2\cdot33}(NH_3)_4Pt^{2\cdot33}\text{-}Cl_4]_n$ $\cdots$ with a Pt–Pt distance $d = c/2 = 2.85$ Å; (ii) Wolffram's type, mixed-valence chlorine bridged chains $\cdots$ $[Pt^{II}(NH_3)_4 \cdots Cl\text{-}Pt^{IV}(NH_3)_4\text{-}Cl]_n \cdots$. The former are responsible for the high conductivity value, while the latter account for the resonance effect in the Raman spectrum and for the N:Pt ratio of our poMgs. Simply, this lattice may be viewed as a Schöllhorn's type lattice in which one chain out of four is a Wolffram's type chain. Further data on the above-mentioned yellow salt are needed in order to investigate a possible relation between the Pt–Pt distance and the mean Pt oxidation state in the Wolffram's type chain.

At this stage more complex structures (and superstructures) cannot entirely be excluded, for instance mixed $\{[Pt(NH_3)_4\text{-}PtCl_4]_x[Pt^{II/IV}(NH_3)_4Cl]_{1-x}\}$ linear chains adjacent to pure $[Pt(NH_3)_4PtCl_4]$ chains, the latter accounting for the high conductivity of the compound.

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