On the Nature of Partially Oxidised Magnus Green †

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The complex $[Pt(NH_3)_4][Pt(NH_3)_4Cl_2][HSO_4]_4$ can be synthesised by the partial aerial oxidation of Magnus green in 50% sulphuric acid. It forms as highly dichroic, orange-red needles, which are shown to contain chlorine-bridged linear chains of the sort $\cdots Pt^{II} \cdots Cl{-}Pt^{IV}{-}Cl \cdots$, the ammonia molecules being co-ordinated in the equatorial positions to each platinum atom. The resonance Raman spectrum of the complex at 80 K, obtained by irradiating within the contour of the intense $Pt^{IV} \longleftarrow Pt^{II}$ intervalence band, is dominated by a progression in ν_1 to $11\nu_1$, where ν_1 is the symmetric $Pt^{IV}{-}Cl$ chain-stretching mode. The thermochromism of the complex is discussed. The nature of the other products of partial oxidation of Magnus green is also discussed.

There is considerable interest in stacked complexes in which the metal atoms have a non-integral oxidation state, since for such complexes a particularly facile mechanism exists for electrical conductance along the chains, *e.g.* as for $K_2[Pt(CN)_4]\cdot 0.3Br\cdot 3H_2O$.[1] The structure of the complex formed by partial aerial oxidation of Magnus green, $[Pt(NH_3)_4][PtCl_4]$, in 50% sulphuric acid is controversial, as highlighted at a recent N.A.T.O. conference.[2] In the initial publication, Gitzel *et al.*[3] reported that the copper-coloured product of the above reaction, formulated as $Pt_6(NH_3)_{10}Cl_{10}(HSO_4)_4$, is a columnar structure in which not only one-sixth of the ammonia but also one-sixth of the chlorine had been replaced by bisulphate. The average oxidation state of the platinum would thus be +2.33, the same as in $K_2[Pt(CN)_4]\cdot 0.3Br\cdot 3H_2O$. The observed physical and optical properties of the complex led the authors to propose the chain structure $\cdots$ *trans*-$[Pt^{II}(NH_3)_2(HSO_4)_2]{-}[Pt^{II}Cl_4]{-}[Pt^{II}(NH_3)_4]{-}$*trans*-$[Pt^{IV}Cl_2(HSO_4)_2]{-}[Pt^{II}(NH_3)_4]{-}[Pt^{II}Cl_4] \cdots$ for the complex. These conclusions were seemingly confirmed by *X*-ray diffraction work by Tsujikawa *et al.*,[4] who showed that the *c* (chain) axis length of the partially oxidised complex is exactly three times that of Magnus green (6.49 Å, implying a Pt–Pt distance of $c/2$ = 3.25 Å), whereas the *a* axis lengths are identical (9.03 Å). The electrical conductivity of the complex is, surprisingly, strongly sample dependent, and $\sigma_{max.}$ peaks at ~190 K with a value in the range 10^{-4}—10^{-1} Ω^{-1} cm^{-1}.

The above structural conclusions are, however, called into question by a brief report[5] on the Raman spectra of the partially oxidised complex and on its bromo-analogue, since the results are only compatible with the formulation involving halogen-bridged chain polymers. A further complication is provided by the galvanostatic anodic oxidation of Magnus green in aqueous H_2SO_4 electrolyte [40—70 wt.%, 300 K] which yields copper-coloured needles thought to be the complex of Gitzel *et al.*, but formulated as $[Pt(NH_3)_4PtCl_4]^{0\cdot 5+}[H_{1\cdot 5}SO_4]^{0\cdot 5-}\cdot xH_2O$; this structure, involving $Pt^{2\cdot 25+}$, has been described as consisting of partially oxidised Magnus green type chains with a Pt–Pt distance of 2.86 Å. Yet a further formulation of a partially oxidized Magnus green, as the chlorine-bridged chain structure $[Pt(NH_3)_4][Pt(NH_3)_4Cl_2][SO_4][PtCl_4]$, suffers from unacceptable analytical characterisation (especially with respect to nitrogen and sulphate analyses).[7]

In view of the obvious problems over the formulation and structural characterisation of partially oxidised Magnus green, we have carried out a synthetic and spectroscopic study of the system. This has led to the complete characterisation of the Wolffram's red analogue $[Pt(NH_3)_4][Pt(NH_3)_4Cl_2][HSO_4]_4$ and to the realisation that it is only one of the products of partial oxidation of Magnus green. At least one other complex is formed which does not have a chlorine-bridged structure but probably direct Pt–Pt bonds akin to those in Magnus green itself. The chlorine-bridged complex has intriguing optical, thermochromic, and resonance Raman spectra which are described in detail below.

Experimental

Preparations.—The complex $[Pt(NH_3)_4][Pt(NH_3)_4Cl_2][HSO_4]_4$ was isolated as orange-red microcrystals by allowing a hot solution of Magnus green dissolved in 50% (v/v) concentrated sulphuric acid and water to cool slowly to room temperature. Large needles were obtained by dissolving the above product in 50% concentrated sulphuric acid and then holding the solution at 60 °C for *ca.* 30 min (Found: H, 2.85; Cl, 7.70; N, 11.1; S, 12.2. $H_{28}Cl_2N_8O_{16}Pt_2S_4$ requires H, 2.85; Cl, 7.20; N, 11.35; S, 13.0%).

Spectroscopic Details.—Electronic spectra were recorded by transmission through Nujol mulls or by diffuse reflectance on a Cary 14 or a Unicam SP800 spectrometer.

Infrared spectra were recorded on a Perkin-Elmer 225 and a Nicolet 7199 interferometer (courtesy of Dr. P. L. Goggin, Bristol).

Raman spectra were recorded by use of a Spex 1401 or 14018 double monochromators. The room temperature spectra were obtained by the spinning sample technique and at *ca.* 80 K by use of a Dewar assembly employing liquid nitrogen. Those at 373 K were obtained by holding the sample on a copper block fitted with two small heaters (RIIC temperature controller). All samples were made by dispersing the compound in $K_2[SO_4]$ because the complex either decomposes or exchanges anion if pressed in KCl, $K[ClO_4]$, or $K[NO_3]$. We observed that the samples made up of the pure complex or in $K_2[SO_4]$ all gave the same spectra. The a_1 mode of the SO_4^{2-} was used as the internal standard for the excitation profile measurements. All band intensities were estimated as the products of peak height and full-width half-maxima (f.w.h.m.) and corrected for the response of the instruments. Band wavenumbers were measured by reference to the emission lines of neon.

Results and Discussion

The results pertaining to the complex $[Pt(NH_3)_4][Pt(NH_3)_4Cl_2][HSO_4]_4$ will be presented and discussed in detail, since this complex could readily be characterised and since it has a number of intriguing spectroscopic properties. The results

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† *catena*-Tetra-ammine-μ-chloro-platinum(II,IV) tetrakis(hydrogensulphate), $[Pt(NH_3)_4][Pt(NH_4)Cl_2][HSO_4]_4$.

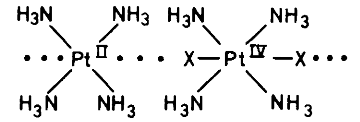
Table 1. Summary of the data on the linear-chain platinum complexes studied

Complex	Crystal colour [a]	Powder colour [b]	i.v. band max./cm^{-1} [c]	e.p. max./cm^{-1} [d]	ω_1/cm^{-1}	x_{11}/cm^{-1}	$\frac{I(2\nu_1)}{I(\nu_1)}$	Progression length (T/K)
$[Pt(NH_3)_4][Pt(NH_3)_4Cl_2][HSO_4]_4$	Orange	Yellow	—	21 000	321.6 ±0.3	−0.79 ±0.03	0.47	11ν_1 (~80)
	Orange	Yellow	19 600 [e]	18 100	317.3 ±0.3	−0.7 ±0.05	0.57	6ν_1 (293)
	Dark red	Red	18 500	16 900	317.8 ±0.5	−2.4 ±0.1	0.29	4ν_1 (373)
$[Pt(NH_3)_4][Pt(NH_3)_4Br_2][HSO_4]_4$ [f]	Gold-green	Purple	17 800 [e]	14 200	175.6 ±0.3	−0.42 ±0.03	0.58	10ν_1 (~80)
$[Pt(NH_3)_4][Pt(NH_3)_4I_2][HSO_4]_3[OH]\cdot H_2O$ [f]	Green-brown	Green	13 600	<12 500	125.0 ±0.3	−0.47 ±0.03	0.55	8ν_1 (~80)

[a] By specular reflectance. [b] By transmission. [c] By diffuse reflectance (i.v. = intervalence). [d] e.p. = Excitation profile. [e] 21 200 cm^{-1} by transmission. [f] Ref. 8.

relating to other species which may be obtained from various sulphuric acid solutions of Magnus green can only be alluded to at this time.

$[Pt(NH_3)_4][Pt(NH_3)_4Cl_2][HSO_4]_4$.—*Electronic spectra.* The large needle-like crystals of this complex are dichroic and have a metallic sheen; they appear orange-red if the electric vector of the incident beam is parallel to the needle-axis, but colourless when it is perpendicular thereto. This behaviour is characteristic of linear-chain halogen-bridged complexes of platinum, and is similar to that of the analogous bromo- and iodo-complexes for which *X*-ray diffraction studies have recently been completed.[8] The bromo- and iodo-complexes have been shown to be Wolffram's red analogues (shown below) and



there is no doubt that, from the spectroscopic results (see below), the chloro-complex is of the same type.

The chloro-complex shows a reversible colour change with change of temperature, being orange-red at room temperature and brick red above 60 °C. The electronic spectrum of the complex is shown in Figure 1, from which it appears that the transmission spectrum (as a Nujol mull) is better resolved than the diffuse reflectance spectra (a not uncommon situation). The latter spectra are, however, easier to record for samples at different temperatures, and it is clear from such spectra that the band maximum of lowest energy for the complex (attributed to the $Pt^{IV} \leftarrow Pt^{II}$ intervalence transition) shifts to lower energies as the temperature of the sample is raised. This was shown not to be due to a change in the water content of the crystals (such as has been noted for some related complexes)[9,10] by holding the complex under reduced pressure at 100 °C for several hours, and then allowing it to cool in vacuum to room temperature; the complex simply reverted to its original orange-red colour. This suggests that the complex undergoes a slight but reversible structural change with change of temperature. The relevant spectral properties of the complex are summarised in Table 1, which also includes some data on the already characterised and analogous bromo- and iodo-complexes.[8]

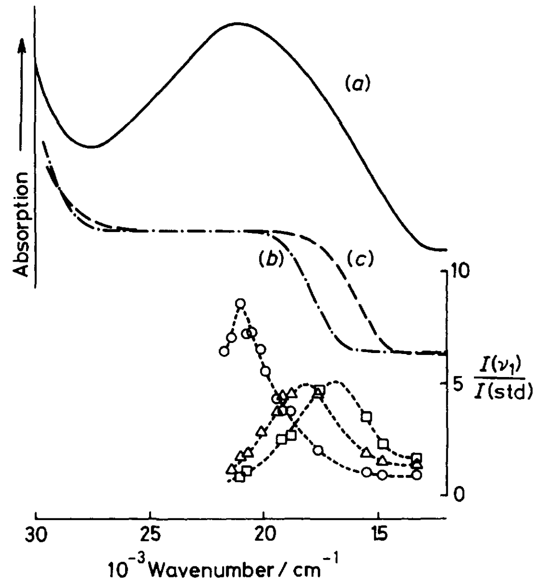


Figure 1. Electronic spectra of $[Pt(NH_3)_4][Pt(NH_3)_4Cl_2][HSO_4]_4$ (*a*) by transmission at 293 K, (*b*) and (*c*) by diffuse reflectance at 293 and 373 K, respectively, together with the excitation profile of the ν_1 band of the complex at *ca.* 80 (○), 293 (△), and 373 K (□); *I*(std) = intensity standard

Infrared spectra. The wavenumbers of bands observed in the i.r. spectrum of the complex (at 293 K) are given in Table 2 together with those of $[Pt(NH_3)_4]Cl_2$[12] and $[Pt(NH_3)_4Cl_2]Cl_2$.[11] The bands arising form the cationic part of the mixed-valence complex bear close resemblance in both wavenumbers and intensities to those of the cationic monomers.

Resonance Raman spectra. Since this complex shows considerable colour change with change of temperature, its resonance Raman spectrum has been recorded at *ca.* 80, 293, and 373 K. Consistent with the shift in the intervalence band with change of temperature, the most striking resonance Raman spectra at each temperature were found for different exciting lines, various blue lines when the complex was at 80 and 293 K, and a yellow line (568.2 nm) when it was at 373 K. The observed band wavenumbers, relative intensities, f.w.h.m., and assignments are given in Table 3.

As for other linear-chain complexes studied,[12] the resonance Raman spectrum of the complex is characterised by a very large enhancement to the intensity of ν_1, the symmetric Pt^{IV}–Cl chain stretching mode, and by the development of a

Table 2. Wavenumbers (cm^{-1}) of bands observed in the i.r. spectra of the complexes

$[Pt(NH_3)_4]Cl_2$ [a]	$[Pt(NH_3)_4Cl_2]Cl_2$ [a]	$[Pt(NH_3)_4][Pt(NH_3)_4Cl_2][HSO_4]_4$ [b]	Assignment
3 250s,br	3 150s,br	3 230s,br	$\nu(NH)$
3 140w,br	3 030s,br		
1 560m	1 530s	1 560s	$\delta(NH_3)_{asym}$
1 325s	1 337s	1 325m	$\delta(NH_3)_{sym}$
		1 275 (sh)	$\omega(NH_2)$
		1 225vs	$\nu_3(HSO_4)$
		1 155vs	
		1 060vs	$\nu_1(HSO_4)$
		966w	
888m	940s	854vs	$\delta(NH_3)_{rock}$
842m		722w	
		608s	$\nu_4(HSO_4)$
	564w	584vs	
510w	524m	510w	$\nu(Pt-N)$
		436m	$\nu_2(HSO_4)$
		427m	
	348m	358s	$\nu(Pt-Cl)_{asym}$
	288s	272vs,br	$\delta(N-Pt-N)$
236m		246s,br	
	167m	160m	$\delta(X-Pt-X)$
150w			
	127s		lattice
118w,br	105s	114w	
		98m,br	

[a] Ref. 12. [b] This work.

Table 3. Wavenumbers, relative intensities, f.w.h.m., and assignments of bands observed in the resonance Raman spectrum of $[Pt(NH_3)_4][Pt(NH_3)_4Cl_2][HSO_4]_4$

$\tilde{\nu}$/cm^{-1}	$I(v_1\nu_1)/I(\nu_1)$	$\Delta\tilde{\nu}_{\frac{1}{2}}$/cm^{-1}	Assignment
(*a*) 457.9 nm at *ca.* 80 K			
107.8			
140.4			
184.2			
220.7			$\delta(N-Pt-N)$
319.2	1.00	11.8	$\nu_1(Cl-Pt^{IV}-Cl)_{sym}$
334.3			
357.6			$\nu_2(Cl-Pt^{IV}-Cl)_{asym}$
436.4			
543.4			$\nu_1 + \delta(N-Pt-N)$
639.7	0.47	23.2	$2\nu_1$
673.2			$\nu_1 + \nu_2$
760.2			$\nu_1 + 436.4$
865			$2\nu_1 + \delta(N-Pt-N)$
956.7	0.27	36.2	$3\nu_1$
993.8			$2\nu_1 + \nu_2$
1 086			$2\nu_1 + 436.4$
1 183			$3\nu_1 + \delta(N-Pt-N)$
1 269.7	0.22	59	$4\nu_1$
1 317			$3\nu_1 + \nu_2$
1 390			$3\nu_1 + 436.4$
1 503			$4\nu_1 + \delta(N-Pt-N)$
1 581.5	0.17	71	$5\nu_1$
1 720			$4\nu_1 + 436.4$
1 815			$5\nu_1 + \delta(N-Pt-N)$
1 892	0.13	95	$6\nu_1$
2 135			$6\nu_1 + \delta(N-Pt-N)$
2 207	0.09	110	$7\nu_1$
2 520	0.05	125	$8\nu_1$
2 810	~0.02	>125	$9\nu_1$
3 120	<0.02	>125	$10\nu_1$
3 420	<0.02	>125	$11\nu_1$
(*b*) 476.2 nm at 293 K ($K_2[SO_4]$disc)			
220.2			$\delta(N-Pt-N)$
316.4	1.00	12.6	ν_1
541.4			$\nu_1 + \delta(N-Pt-N)$
629.2	0.57	28.3	$2\nu_1$
860.4			$2\nu_1 + \delta(N-Pt-N)$
944.3	0.36	46	$3\nu_1$
1 251.9	0.21	55	$4\nu_1$
1 567	0.17	71	$5\nu_1$
1 878	0.10	~86	$6\nu_1$
(*c*) 568.2 nm at 373 K ($K_2[SO_4]$ disc)			
220.3			$\delta(N-Pt-N)$
313.5	1.00	17	ν_1
353.6			ν_2
540			$\nu_1 + \delta(N-Pt-N)$
620.9	0.29	40	$2\nu_1$
925	0.1	~75	$3\nu_1$
1 225	<0.1		$4\nu_1$

long overtone progression in ν_1 as far as $11\nu_1$. Subsidiary progressions of the sort $v_1\nu_1 + \nu_x$ are also observed, where ν_x is another Raman-active mode (*e.g.* that at 220 cm^{-1} attributable to a NPtN bend). Thus the progressions $v_1\nu_1 + \delta(NPtN)$ and $v_1\nu_1 + 2\delta(NPtN)$ reach, at resonance, $v_1 = 6$ and 3, respectively.

The best resonance Raman spectra at 293 and 373 K are almost identical with that at 80 K (shown in Figure 2) except that the $v_1\nu_1$ progression is shorter at higher temperatures (reaching only $v_1 = 6$ and 4, respectively) and so also is the $v_1\nu_1 + \delta(NPtN)$ progression (reaching only $v_1 = 2$ and 1, respectively). The close similarity between the spectra at the three temperatures indicates that any structural change on change of temperature can only be slight. There is, however, a slight decrease in ν_1 with increase in temperature, from 319.2 (~ 80 K) to 316.4 (293 K) to 313.5 cm^{-1} (373 K), *cf.* the corresponding mode, $\nu_{sym}(Cl-Pt^{IV}-Cl)$, of the free ion $[Pt^{IV}(NH_3)_4Cl_2]^{2+}$ occurs at 338 cm^{-1}.[12] The direction of this ν_1 band shift, as well as the direction of the shift of the intervalence band maximum, both indicate that, on the basis of previously established correlations,[13] the bridging chlorine atom moves more towards the central position between the Pt^{II} and Pt^{IV} atoms with increasing temperature. It is noteworthy, in this context, that the $\delta(NPtN)$ mode shows no significant wavenumber change with change of temperature (220.5 ± 0.3 cm^{-1} at all measured temperatures).

The observation of long overtone progressions permits [14] the calculation of approximate values for the harmonic band wavenumber, ω_1, and anharmonicity constant, x_{11}. The results of such analyses on the three data sets are included in Table 1, from which it is apparent that ν_1 is almost exactly a simple harmonic oscillator at 80 or 293 K. The apparent value of x_{11} increases from -0.7 to -2.4 cm^{-1} at 373 K, a feature which almost certainly arises from band distortion as a consequence of hot band contributions to the intensities; this is also the implication behind the obvious increase in full-width half-maxima of the members of the $v_1\nu_1$ progression with increase in temperature (Table 2).

The excitation profile of the ν_1 band maximizes near the low wavenumber edge of the intervalence band maximum, a typical result for this type of complex.[11] Moreover, it clearly moves to lower wavenumber (Figure 1) as the temperature of the sample is raised (21 000 at *ca.* 80 K, 18 100 at 293 K, and 16 900 cm^{-1} at *ca.* 373 K). This confirms the conclusions of the electronic spectral work and of the ν_1 band shifts with change of temperature, *i.e.* that the equilibrium position of

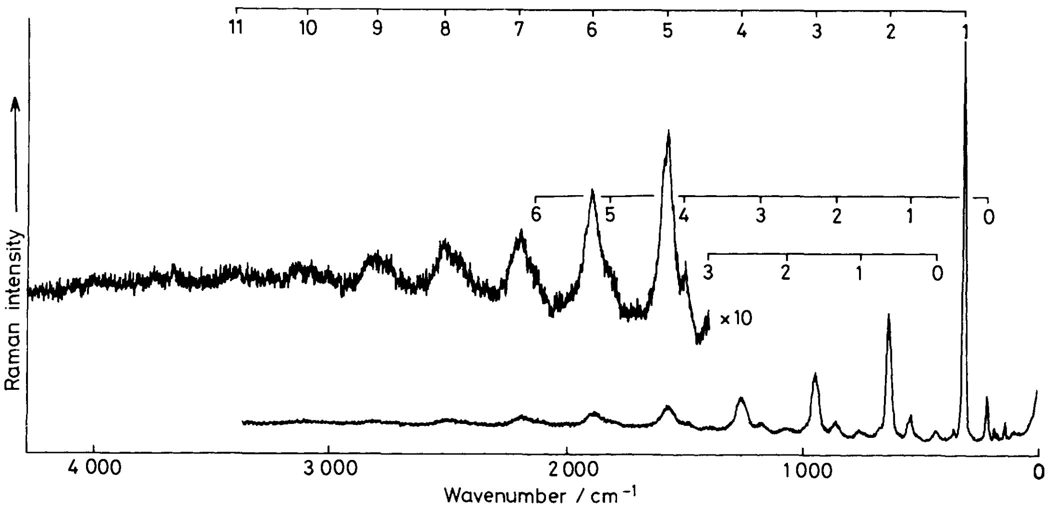


Figure 2. Resonance Raman spectrum of $[Pt(NH_3)_4][Pt(NH_3)_4Cl_2][HSO_4]_4$ at *ca.* 80 K (λ_0 = 457.9 nm, slit width 4 cm^{-1})

the bridging chlorine becomes more centrally placed at higher temperatures.

Other Species derived from Partially Oxidised Magnus Green.—The synthetic work has established that, under the conditions employed, $[Pt(NH_3)_4][Pt(NH_3)_4Cl_2][HSO_4]_4$* is the final product in the oxidation of Magnus green. But despite several attempts we have been unable to characterise the copper-coloured intermediate products, the analyses for which (like the electrical conductance) [4] are irreproducible (as noted by others).[15] Indeed, it seems probable that there are several other products of the partial oxidation of Magnus green, and that these possess direct Pt–Pt bonds. Certainly none of these products gives an identifiable Raman spectrum, and none gives any evidence for halogen bridging.

Acknowledgements

We thank the S.R.C. and the University of London for financial support, and Johnson Matthey Ltd. for the loan of chemicals.

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Received 29*th April* 1982; *Paper* 2/706

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* *Note added in proof.* The *X*-ray crystal structure of $[Pt(NH_3)_4][Pt(NH_3)_4Cl_2][HSO_4]_4$, prepared by H_2O_2 oxidation of $[Pt(NH_3)_4]Cl_2$ in 50% (v/v) H_2SO_4, has just been published (P. E. Fanwick and J. L. Huckaby, *Inorg. Chem.*, 1982, **21**, 3067), confirming the conclusion of the present paper that the material is a linear-chain mixed-valence complex. It is isostructural with the analogous bromide.[8] The $Pt^{II} \cdots Cl\text{-}Pt^{IV}$ angle at room temperature (176.2°) is possibly temperature dependent, and this could account for the thermochromism of the complex. The electronic spectrum of the chloro-complex reported by Fanwick and Huckaby is invalid since it was obtained from a KBr disc, in which medium halogen exchange as well as anion exchange takes place (see Experimental section). Our observed intervalence band maximum for the chloro-complex (19 600 cm^{-1} by transmission as a Nujol mull at 293 K) is similar to that recently calculated for this complex (*ca.* 24 000 cm^{-1}) by extended Hückel methods (M.-H. Whangbo and M. J. Foshee, *Inorg. Chem.*, 1982, **20**, 113).