Synthesis and magnetic characterization of *trans*-dichloroplatinum blues with creatinine

E. Coronado*, C. J. Gómez-García

Dept. Química Inorgánica, Facultad de Química, Universidad de Valencia, Dr Moliner 50, 46100 Burjassot (Spain)

F. J. Martín-Gil and J. Martín-Gil*

Dept. Química Inorgánica, ETSII, Universidad de Valladolid, Paseo del Cauce, 47011 Valladolid (Spain)

Abstract

By reaction of *trans*-$[Pt^{II}Cl_4]^{2-}$ with the amidate ligand creatinine two new paramagnetic blue platinum complexes have been obtained, namely violet and green varieties. These complexes have been characterized from thermal analysis, EPR and magnetic susceptibility. The violet complex has been formulated as *trans*-$[Pt(creat)(H_2O)Cl]_4Cl$. This compound has shown to be very stable, showing an extensive hyperfine structure in the powder EPR spectra. This result is a clear evidence of a tetranuclear oligomeric structure with one delocalized unpaired spin in the unit. EPR spectra in frozen solutions indicate that this mixed-valence complex maintains its oligomeric structure upon dissolution in water. Finally, magnetic susceptibility measurements of this platinum blue, over the range 4.2–300 K, show an unusually high magnetic moment, which varies from 4.5 μ_B at room temperature to 1.1 μ_B at 4.2 K.

Introduction

Blue platinum complexes have attracted the interest of many chemists due to their unusual colors, paramagnetic properties and potential antitumor activity [1–4]. These species are mixed-valent, metal–metal bonded and ligand-bridged oligomers. For example, the structure of one of these products, the *cis*-diammine-platinum a-pyridone blue, revealed the presence of a tetranuclear zigzag chain [5]. Moreover, due to the non-integral oxidation state of the platinum atoms these species exhibit EPR signals in powder as well as in frozen solutions [3, 4, 6]. The spectral pattern is quite often restricted to two broad bands, but in some cases extensive hyperfine structures due to the coupling of the delocalized electron with ^{195}Pt have been observed [6]. These may provide information about the extent of electronic delocalization over several platinum atoms.

Here we present the synthesis and magnetic characterization of the blue complexes obtained by reaction of *trans*-$[Pt^{II}Cl_4]^{2-}$ with the amidate ligand creatinine.
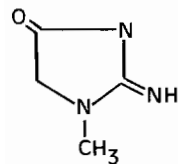
*Authors to whom correspondence should be addressed.

Experimental

Syntheses

Two different solid samples of *trans*-dichloro-platinum creatinine blue, namely green and violet varieties, were isolated by the following method. A total of 415 mg (1 mmol) of K_2PtCl_4 was dissolved in 20 ml of water, and 226 mg (2 mmol) of creatinine was added to yield a yellow solution. *trans*-$Pt(creat)_2Cl_2 \cdot 2H_2O$ precipitated immediately and was filtered and washed. By heating this complex in the minimum amount of water, at 40 °C for 1 h and in the dark, gradual color changes of the solution from green to violet, and simultaneous precipitation of the corresponding coloured powders, were observed. The analysis of the green compound gave stoichiometries that vary from batch to batch, whereas the analysis of the violet crystalline powder led to the accurate assignation of the formula $[Pt(creat)(H_2O)Cl]_4Cl$. *Anal.* Calc. for $[Pt(C_4H_7N_3O)(H_2O)]_4Cl_5$: C, 12.95; H, 2.45; N, 11.34; Pt, 52.65; H_2O, 4.86. Found: C, 13.62; H, 2.52; N, 12.14; Pt, 52.2; H_2O, 4.90%. The water was determined by thermal analysis using Perkin-Elmer 3600 and DTA 1700 instruments. Such analysis also emphasized the larger thermal stability of this compound compared with that of the starting material *trans*-$Pt(creat)_2Cl_2 \cdot 2H_2O$. Thus, while the decomposition peak of the violet product to give
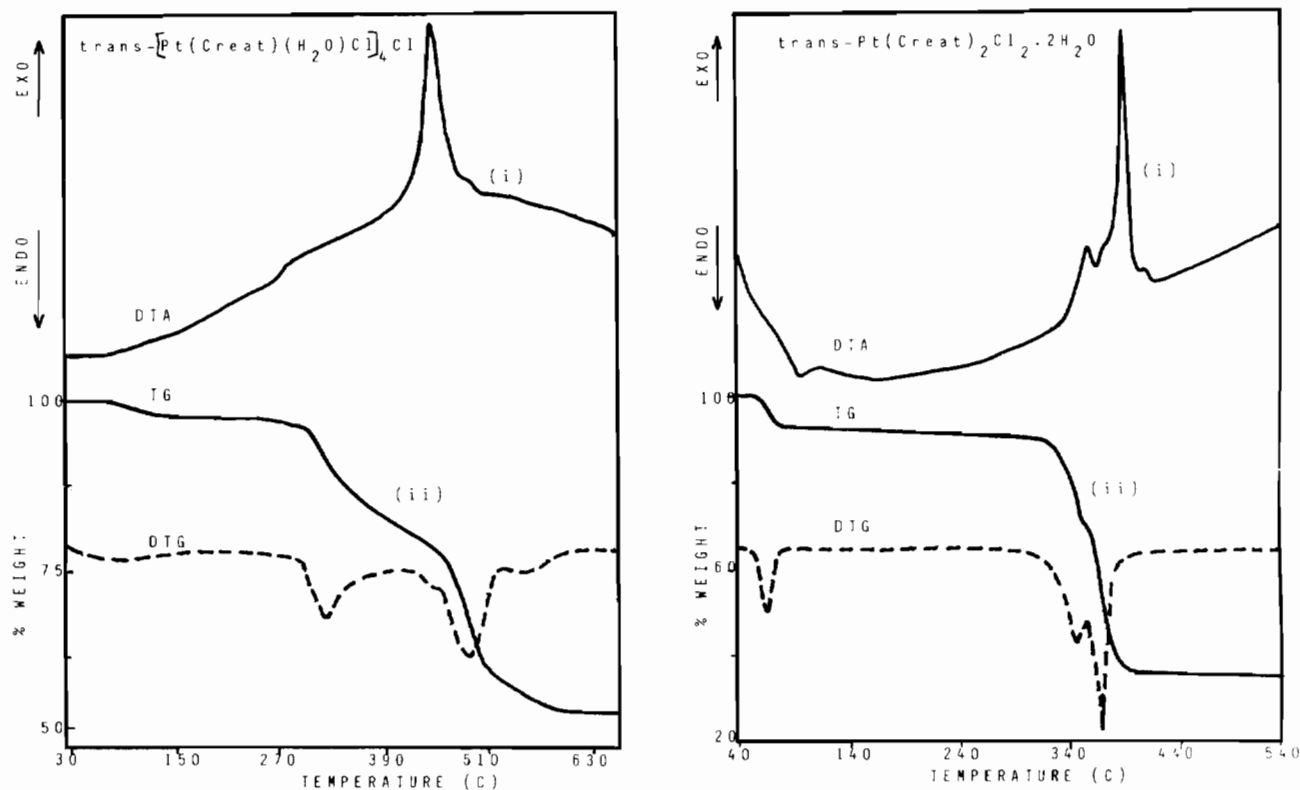
Fig. 1. Comparison of the thermal stability of the violet compound *trans*-[Pt(creat)(H₂O)Cl]₄Cl with that of the starting material *trans*-Pt(creat)₂Cl₂·2H₂O. The DTA and TG-DTG studies were carried out in air (i) and nitrogen (ii), at a heating rate of 10 °C/min.

Pt was observed in DTG at 480 °C, for the starting material it was observed at 370 °C (Fig. 1).

EPR measurements

The X-band EPR spectra of powdered samples were recorded on a Bruker ER 200D spectrometer at both room temperature and 100 K. The EPR spectra of frozen aqueous solutions were recorded at 100 K.

Magnetic measurements

Magnetic susceptibility data were carried out in the temperature range 2–298 K with a magnetometer 905-VTS (S.H.E. Corporation), equipped with a SQUID sensor.

Results and discussion

EPR measurements

The powder EPR spectrum of the violet complex shows an axial spectrum with an extensive hyperfine structure (Fig. 2(a)). This spectrum remains essentially unchanged upon cooling down. The perpendicular component of g is centered at $g_\perp = 2.43$, while the parallel component is at $g_\parallel = 1.96$. The hyperfine structure is

better resolved on $g_\perp$, in which as many as nine signals with a uniform separation of *c.* 80 G are clearly discernible. In turn, very weak signals are seen on $g_\parallel$. The type of spectrum observed in this compound is a clear evidence of its oligomeric structure in the solid state, as has been previously pointed out in other blue platinum complexes [3, 4, 6]. Thus, the large anisotropy of the g tensor and the fact that $g_\perp > g_\parallel$ support that the unpaired electron resides in a d_{z^2}-type molecular orbital, which is directed along the platinum chain axis. On the other hand, the extensive hyperfine structure is consistent with the delocalization of one unpaired electron (actually one unpaired hole) over several platinum centers. Due to the presence of a mixture of ¹⁹⁵Pt ($I = 1/2$, natural abundance 33.7%) and spinless platinum isotopes, the observed spectrum can be viewed as the sum of several subspectra that correspond to the various isotopic contributions. In fact, an approximately nine-line hyperfine splitting is expected for a tetranuclear oligomer with one delocalized hole [4]. Hence, the EPR spectra of the violet compound constitute a clear evidence for a tetranuclear structure. This result is in good agreement with the proposed chemical formula (see 'Experimental'), which involves a non-integer platinum oxidation state of 2.25. On the other hand, the polymeric structure of the platinum
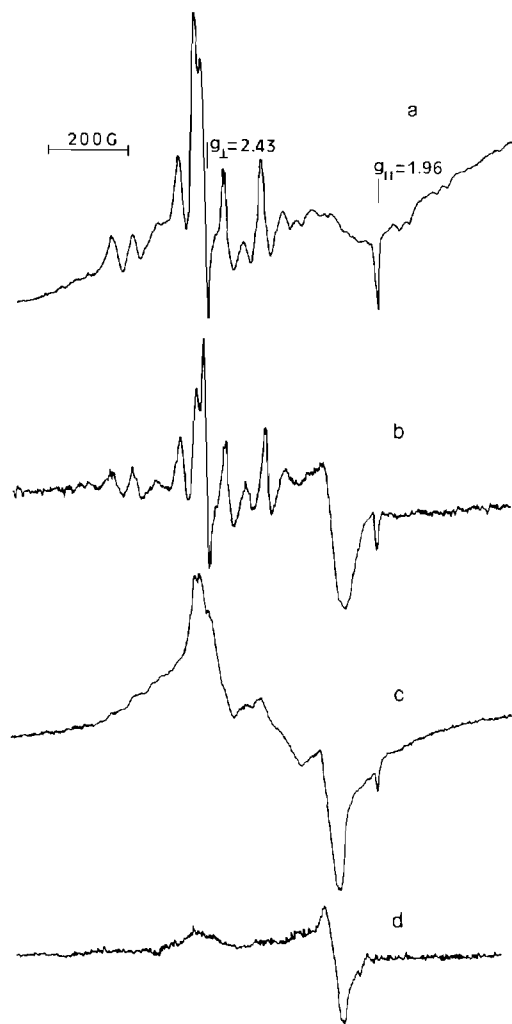
the signals associated to platinum blue complexes (centered at $g \approx 2.43$ and $g = 1.96$) an intense signal at $g \approx 2.06$. This observation suggests that the green compound contains a mixture of a mixed valent oligomer and a paramagnetic impurity. The fact that the g value of this impurity is close to that associated with the hydrolysis product of the violet complex, suggests that both the paramagnetic impurity and the hydrolysis product have in fact the same nature. That is supported by the EPR spectra of the green complex in frozen solution, which exhibit only the signal associated with the hydrolysis product. This observation indicates that the green compound readily decomposes in solution.

Magnetic measurements

The EPR features of the violet compound are in agreement with the presence of one odd electron delocalized over a tetranuclear platinum unit with a mean oxidation state of the platinum atoms of 2.25. In order to obtain information on the magnetic moment of this unit we have studied the magnetic properties of the compound. The effective magnetic moment per unit is of $c.$ 4.5 μ_B at room temperature. This value is significantly larger than that expected from the presence of one unpaired electron electron (a value of 1.81 μB per tetranuclear unit has been found in the cis-diammine-platinum a-pyridone blue [4]). However, due to the high spin–orbit coupling of Pt^{III} and to the lack of structural data, the relation between the value of the magnetic moment and the number of unpaired electrons cannot be easily established in this kind of system. In fact, values of 6.93 μ_B per platinum atom have been reported for uracil platinum blues [7].

Another unusual result deals with the temperature dependence of the magnetic moment, which shows a continuous decrease from $c.$ 4 μ_B at 120 K to $c.$ 1 μ_B at 5 K (Fig. 3). This behavior might be related with (i) the presence of antiferromagnetic exchange interactions between the oligomeric units or (ii) the effect of spin–orbit coupling on the ground state of Pt^{III}. The
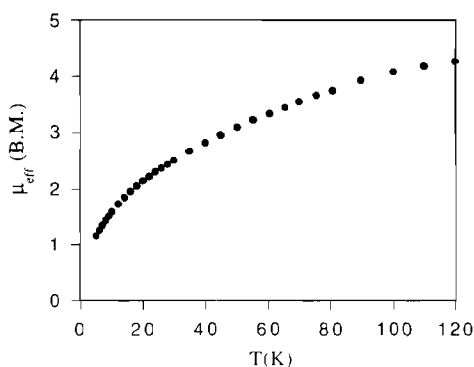

Fig. 2. X-band EPR spectra of violet and green varieties of the creatinine platinum blues. (a) Powder sample of the violet compound at room temperature; (b) frozen aqueous solution of the violet compound at 100 K; (c) powder sample of the green compound at 100 K; (d) frozen aqueous solution of the green compound at 100 K.

compound supports the larger thermal stability of this, compared with that of the monomeric starting material $trans$-Pt(creat)$_2$Cl$_2 \cdot 2H_2O$.

With respect to the stability of the violet complex in aqueous solution, we notice that the EPR spectrum remains almost unchanged in aqueous frozen solution (Fig. 2(b)), indicating that the oligomeric structure is retained. However, the appearance of a large and unfeatured signal centered at $g = 2.06$, which increases with time, indicates that this compound decomposes slowly in solution.

The EPR spectra of the green compound from both powder and frozen solution are displayed in Fig. 2(c) and (d). These are much less informative than those of the violet compound. In the solid state the spectra are temperature independent and show, together with

Fig. 3. Magnetic behavior of the violet compound $trans$-[Pt(creat)(H$_2$O)Cl]$_4$Cl.

exchange interactions should cause an averaging of the EPR signals not observed in the powder spectra; hence, the second factor seems to be the one responsible for the observed behavior.

Acknowledgements

References

1 S. J. Lippard, in D. B. Brown (ed.), *Mixed Valence Compounds: Theory and Applications in Chemistry,* Reidel, New York, 1980.
2 P. J. Bednarski, E. Ehrensperger, H. Schonenberger and T. Burgemeister, *Inorg. Chem., 30* (1991) 3015.
3 K. Matsumoto, K. Takahashi and T. Watanabe, *Inorg. Chim. Acta, 121* (1986) L29; K. Matsumoto and T. Watanabe, *J. Am. Chem. Soc., 108* (1986) 1308.
4 J. K. Barton, C. Caravana and S. J. Lippard, *J. Am. Chem. Soc., 101* (1979) 7269.
5 J. K. Barton, D. J. Szalda, H. N. Rabinowitz, J. V. Waszczak and S. J. Lippard, *J. Am. Chem. Soc., 101* (1979) 1434; J. K. Barton, H. N. Rabinowitz, D. J. Szalda, J. V. Waszczak and S. J. Lippard, *J. Am. Chem. Soc., 99* (1977) 2827.
6 P. Arrizabalaga, P. Castan, M. Geoffroy and J. P. Laurent, *Inorg. Chem., 24* (1985) 3656.
7 E. I. Lerner, *Ph.D. Thesis,* Columbia University, NY, 1977.