Inorganica Chimica Acta, *155* (1989) 105–111

Polynuclear Platinum Complexes Deriving from Squaric Acid

RÉGIS SOULES, ALAIN MOSSET, JEAN-PIERRE LAURENT, PAULE CASTAN*
*Laboratoire de Chimie de Coordination du CNRS**, 205 route de Narbonne, 31077 Toulouse Cédex, France*
GÉRALD BERNARDINELLI
Laboratoire de Cristallographie X, 24 quai E. Ansermet, 1211 Geneva, Switzerland
and MICHEL DELAMAR
Institut de Topologie et de Dynamique des Systèmes (ITODYS), Université de Paris VII, 1 rue Guy de la Brosse, 75005 Paris, France

(Received May 30, 1988)

Abstract

The squarate ion $(C_4O_4)^{2-}$ does not substitute for chlorine in $K_2[PtCl_4]$ or in $(NH_3)_2PtCl_2$ but it reacts with the '*cis*-dichlorodiammine hydrolysis products' to yield two complexes. The first one (**I**) can be described from the results of an X-ray diffraction study as a tetranuclear chain of platinum atoms bridged by squaric anions. The second one (**II**) is an amorphous blue compound with the platinum atom in a formal oxidation state of 2.5. A structure involving dinuclear entities is proposed for **II** on the basis of XPS, EPR and LAXS analysis. Oxidation of **I** by nitric acid in the presence of X^- ($X^- = Cl^-$ or Br^-) generates products **IV** and **V** involving an oxidation of 3.0 for platinum. Considering the whole set of complexes derived from squaric acid points to significant similitudes with the 'amide platinum blues'.

Introduction

The interest given to the 'platinum blues' was first originated in their unusual colour [1] and then was sparked by the discovery that some of these products, the 'platinum pyrimidine blues', had proved effectiveness as antitumor agents with low associated nephrotoxicity [2]. Earlier studies suggested a paramagnetic, mixed-valent, oligomeric nature [3]. A more precise description was gained when Lippard *et al.* [4, 5] succeeded in obtaining crystalline *cis*-diammineplatinum α-pyridone blue (abbreviated as PPB in the following) and revealed its tetranuclear amidato-bridged chain structure. In fact, this complex is best described as a dimer of dimers due to the occurrence of two different Pt...Pt distances. Finally, the platinum blues[†] may be considered as members of the large family of compounds having a metallic chain with a non-integral oxidation state of the metal centres and displaying anisotropic properties. Partial removal of d_{z^2} electrons (z axis taken along the mean Pt chain) from the metallic atoms likely improves d_{z^2} orbitals overlap and increases metal–metal interaction through a shortening of the metal–metal distance, and may result in metallic or semi-metallic behaviour. Independently of possible electrical properties, these complexes are expected to display a variety of cooperative or localized magnetic properties. Actually, the platinum blues generally exhibit an ESR signal.

In some instances, when well-resolved hyperfine structures are observed, a good agreement between the experimental and calculated ESR spectra was obtained by assuming coupling of an unpaired electron with the four ^{195}Pt nuclei involved in a tetrameric structure [6]. Basically identical tetranuclear structures have been reported for several complexes with different platinum oxidation states (from 2.0 to 3.0) but all involving amidato ligands [7–9]. To our knowledge, there are few reports of blue species involving other types of ligands. Phosphate bridging has been suggested for amorphous $H_n[Pt(NH_3)_2(PO_n)]0.5H_2O$ [10], whereas sulphate bridges would occur in the blue product originating from UV irradiation of *cis*-$[Pt(NH_3)_2(H_2O)_2]SO_4$ [11]. A blue compound, $[Pt(C_6Cl_5)_4]^-$, has been recently reported and structurally characterized as a mononuclear Pt(III) complex [12].

The present paper is devoted to platinum complexes involving squaric acid as ligand. From a liter-

---

*Author to whom correspondence should be addressed.
**Unité No. 8241, liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique.

[†] The calling 'platinum blue' without other specification is used in this paper for the amide-bridged platinum blue compounds.

0020-1693/89/$3.50

ature survey, it appears that two related complexes have been previously mentioned: a dinuclear platinum(II) complex with squarato-1,2 bridges [13] and a black compound whose formulation, $K_{1.6}[Pt(C_4O_4)_2]\cdot 2H_2O$ [14], suggests that the platinum atom has a formal oxidation state of 2.4. The latter species, which has not been structurally characterized, is reported to be semiconducting.

We will describe the syntheses, crystal and amorphous structure, magnetic properties, UV–Vis spectra of the following compounds: green crystalline $[Pt(NH_3)_2(C_4O_4)]_4$ (**I**), blue amorphous $[Pt(NH_3)_2(C_4O_4)]_n(C_4O_4)_{n/4}$ (**II**) and red $[Pt(NH_3)_2(C_4O_4)]_2X_2$ (X = Cl, Br) (**IV**) and (**V**) and compare their properties with those of the *cis*-diammine platinum α-pyridone analogue.

Results and Discussion

Syntheses

As previously noted, the possibilities of preparing tetranuclear blue platinum complexes are essentially restricted to amidato ligands. Therefore, it is interesting to search for new ligands able to yield disposition similar to that of α-pyridone.

One of the aims of the present paper is to show that squaric acid offers the opportunity of developing a chemistry similar to that of α-pyridone. Indeed, we report on several highly coloured complexes which contain platinum atoms with a formal oxidation state ranging from 2 to 3.

From the reaction of two moles of squaric acid with one mole of '$[Pt(NH_3)_2(H_2O)_2]^{2+}$', two complexes may be isolated: a green microcrystalline species **I** and a blue amorphous species **II**. According to chemical analysis data, they display different values of the molar ratio platinum/squaric acid, *i.e.* 1 and 1.25 for **I** and **II**, respectively. This suggests that the oxidation state of the platinum atoms increases from 2 in complex **I** to 2.50 in complex **II**.

Interestingly, complex **II** can be prepared by reacting complex **I** with an excess of squaric acid which therefore acts not only as a complexing agent but also as an oxidizing agent. When the oxidation of **I** is performed by halogens, red complexes are obtained. On the basis of the analytical data, they likely contain platinum atoms in an oxidation state of 3 and they would result from oxidative addition of halogen atoms to the dimeric unit of complex **I**.

Halogen-capped binuclear Pt(III) complexes can be readily generated through oxidative addition to the tetranuclear platinum(II) complound. Formation of a Pt–Pt single bond apparently drives these binuclear oxidative additions [15]. Simple theory predicts that two Pt–Pt dσ* electrons are transferred to X_2. This is in accordance with the Pt–Pt bond shortening always observed in the binuclear Pt(III)–Pt(III) complexes compared to their Pt(II)–Pt(II) analogous (*vide infra* and Table 2). We have obtained the products of halogen oxidative–addition reactions, **IV** and **V**, as red microcrystals. Apparently, a number of other oxidants (H_2O_2, IO_3^-) also convert Pt(II) to Pt(III) in the presence of nucleophiles X^-. However, all the products are not so well characterized. Single crystals large enough to allow structural X-ray determination have not been obtained. Finally, as described by Toflund [14], an amorphous black species may be isolated from a reaction mixture prepared from tetraaquaplatinum(II) solution and squaric acid. The analytic data are consistent with the presence of $[Pt^{2.3}]$ in this complex.

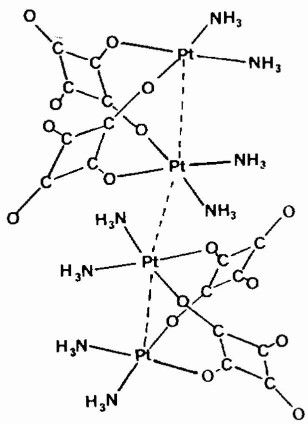

Fig. 1. Structure of complex I.

Structural Study

A preliminary report of the structure of complex **I** has been given elsewhere [16]. Therefore we only recall its main features. In this structure, each platinum atom is coordinated by two ammine ligands in the *cis* position and two oxygen atoms of two squarato dianions. Two quasi planar $Pt(NH_3)_2$ units are bridged by two squarato ligands through their O(1) and O(2) oxygen atoms (Fig. 1) resulting in a dinuclear unit with a Pt(1)–Pt(2) distance of *ca.* 3.162 Å. The coordination planes are not strictly parallel but are canted at an angle of 12°3′, together with a 38° torsional twist about the Pt(1)–Pt(2) bond axis in the bridged binuclear units.

Moreover, two dimeric units are linked through a crystallographic centre of inversion by a Pt(1)...Pt(1′) distance of 3.197 Å so that the overall structure can be viewed as a dimer of dimer with a zig-zag chain of four platinum atoms with a Pt(2)–Pt(1)–Pt(1′) angle of 168°.

This feature is strongly reminiscent of that reported for the blue compounds derivated from amidate-bridged ligands. However it may be underlined that in the case of **I**, the Pt–Pt distances are significantly longer. Bridging 1,2-squarato units are also observed in the dinuclear platinum complex described by Toflund [14] which presents a large Pt...Pt separation of 5.09 Å between dimeric units.

Due to its amorphous nature, complex **II** is not amenable to single crystal X-ray analysis so that we made use of LAXS (Large Angle X-ray Scattering) technique, using recent progress in instrumentation and software (the LASIP system developed in our Laboratory). Owing to the presumed oligomeric structure of **II**, the LAXS technique is seemingly more appropriate than the EXAFS one, which generally gives informations restricted to the first and second coordination spheres around the central atom.

Two samples of complex **II** have been submitted to LAXS analysis. Surprisingly, the related radial distribution curves are not entirely identical. Indeed, in both samples, two maxima are observed at the same positions, *i.e.* 2.06 and 3.05 Å, but the third one is located at 3.44 Å in the first sample and at 3.80 Å in the second one. It may be recalled that the two samples display very similar infrared, UV–Vis and ESCA spectra and yield identical microanalytical data.

All attempts to fit the experimental distributions to a tetranuclear model or to an infinite chain of dinuclear unit failed, leading to the conclusion that complex **II** has to be considered as a dinuclear complex with a Pt(1)–Pt(2) distance of 3.05 Å and a separation between the dinuclear units which varies depending on the sample. Interestingly, the Pt(1)–Pt(2) distance in **II** is significantly shorter than the value observed for complex **I** (3.2 Å).

The proposed structure for **4** and **5** is given in Fig. 2.

X-ray Photoelectron Spectroscopy

XPS is expected to provide valuable informations relating to the oxidation states of the metal in complexes **I** and **II**. For both complexes, the profile of the lines of the Pt_{4f} spectrum shows the existence of only one oxidation state at least on the XPS time scale since, in both cases, the Pt_{4f} is a single doublet. From data obtained on a number of Pt^{2+}, Pt^{4+} [17] and also for additional pairs of Pt^{2+}–Pt^{4+} complexes [18], it is clear that the Pt_{4f} binding energies of Pt^{4+} species are between 2 and 3 eV higher than those of their Pt^{2+} analogues. In the case of *cis*-$(H_3N)_2PtCl_4$, the binding energies are higher by ~2.5 eV than those of *cis*-$(H_3N)_2PtCl_2$ [18]. The energy shift observed when one goes from **I** to **II** gives evidence that there is a significant difference in the oxidation state of the two complexes. As there is no doubt concerning the presence of Pt^{2+} in complex **I**, the most interesting feature of the present data is the increase of binding energy by *ca.* 0.8 eV in going from **I** to **II**. This would be consistent with an oxidation state lying between +2 and +3 for the platinum atom in complex **II**. It may be underlined that in the XPS investigation of the first structurally characterized platinum blue, *i.e.* the α-pyridone blue, the Pt_{4f} binding energies were found to be similar to those exhibited by Pt^{2+} complexes [5].

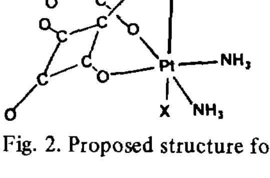

Fig. 2. Proposed structure for complex IV or V.

Magnetic Properties

Static susceptibility measurements show complexes **I**, **IV** and **V** to be diamagnetic and complex **II** paramagnetic. In the latter instance, variation of the applied magnetic field causes a slight but significant amount of ferromagnetism to be detected. Similar observations have been previously reported for the α-pyridone blue [6], the uracil blue [19], the acid-amine blues [20] and it has been generally concluded that this ferromagnetism was attributable to impurities. After correcting for ferromagnetism, a moment of 2.5 BM was obtained for a dinuclear unit of complex **II**. As previously mentioned, this value is hardly related to the oxidation state of the metal. Indeed, ESR data points to the occurrence of a high spin–orbit coupling so that the moment value cannot be directly interpreted in terms of number of unpaired electrons. It may be underlined that a value of 2.5 BM has been recently observed for a genuine mononuclear platinum(III) compound [12] and considered as characteristic of a spin 1/2 system with a large orbital contribution. However, for the $(Pt^{2.25})_4$ complexes, moment values of 1.8 and 1.9 BM have been reported [21]. They are consistent with the presence of one unpaired electron per tetranuclear unit without significant orbital contribution.

Complex (**II**) yields a characteristic ESR spectrum showing two signals devoid of any discernible structure in the $\Delta M = 1$ region. Highly anisotropic g values are obtained, $g_{\parallel} = 1.98$ and $g_{\perp} = 2.36$, as it is generally the case for the platinum blues. This anisotropy and the fact that $g_{\perp} > g_{\parallel}$ allows a description in terms of a d_{z^2} hole state with an admixture of lower lying d_{yz}, d_{xz} states due to spin–orbit coupling. A point of importance was the appearance of an additional signal of weak intensity at $g = 4.3$. It results from a 'half-field' $\Delta M = 2$ transition and points to an interaction between magnetic centres. The profile of the $\Delta M = 1$ signals which are characteristic of a doublet state and the lack of fine structure suggest that the interactions are operative between dinuclear units and are mainly dipolar in character. From the value of the resonance field of the $\Delta M = 2$ transition, a zero-field splitting of *ca.* 0.04 cm^{-1} may be evaluated [22]. In the point-dipole approximation [23], this value would roughly correspond to a dipole–dipole separation of *ca.* 3.6 Å.

Due to the approximations, this value does not significantly differ from the value evaluated in the range 3.4–3.8 Å deduced from structural data and supports the hypothesis of a slight dipolar interaction between adjacent dimeric units. Complexes **IV** and **V** are ESR silent.

Infrared Spectroscopy

Infrared spectra of squarate-containing complexes are quite characteristic of the mode of coordination of the ligand. Complexes like $Ni(C_4O_4)\cdot 2H_2O$ [24], in which the squarate entity is coordinated through all four oxygen atoms, exhibit a strong, broad absorption centred around 1500 cm^{-1}. This has been assigned to a mixture of $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ and $\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ stretching vibrations. For complexes involving the 1 and 3 coordination sites, ill-resolved absorptions are also reported in the 1480 cm^{-1} part of the spectra [25]. In contrast, with the squarate bonded in a 1 and 2 coordination mode, two additional bands are generally observed in the same region, in relation with the presence of localized C=C and C=O bonds.

The infrared bands attributable to the squarate moiety in the region 1450–1800 cm^{-1} for the platinum complexes are listed in Table 1. The position and intensities of the bands in this region are remarkably similar for all the complexes, indicating that these complexes are all bonded in the same 1 and 2 bidentate mode with two uncoordinated oxygen atoms. Finally, frequencies for Pt–Cl (340 cm^{-1}) and Pt–Br (240 cm^{-1}) were obtained for compounds **IV** and **V**.

Electronic Spectroscopy

The diffuse reflectance spectrum of **II** displays two broad, ill-defined absorptions in the ranges 800–600 nm and 600–200 nm respectively.

The first absorption band is at 675 nm with a shoulder at *ca.* 630 nm. The maximum of the second absorption cannot be well-defined but two shoulders are discernible at *ca.* 480 and 570 nm, the latter being more intense than the former.

This spectrum offers some similitudes with those of α-pyridone blue (PPB) and related blue complexes which are dominated by two bands at 680 and 480 nm, less intense absorptions being observed at 800, 550, 480 and 400 nm.

Interestingly, it has been demonstrated that in the case of PPB the transition at 680 nm is characteristic of a tetranuclear structure [2]. Therefore, an analogous absorption is not to be expected in the case of **II** since the LAXS data suggest that this complex would be better described in terms of isolated dinuclear species. So, it seems that the absorption at 675 nm for **II** responsible for the blue colour of this complex, cannot be used to determine a tetrameric structure. Unlike the 680 nm band, the 480 nm absorption in the PPB spectrum does not require a tetrameric structure since it is described as $(Pt_1{-}Pt_2)_\pi \rightarrow (Pt_1{-}Pt_2)_{\sigma*}$. It may have its conterpart in the **II** spectrum with a possible shift due to the lengthening of the Pt–Pt distance and/or the increase of the oxidation state of the platinum atoms. In a recently reported $Pt^{2.5}$ tetranuclear complex with short Pt–Pt distances of *ca.* 2.7 Å this transition seemingly occurs at 478 nm. The band at 580 nm for **II** where Pt–Pt distance is 3.05 Å can be attributed to this transition. Finally, in the UV–Vis reflectance spectra of **IV** and **V** a band in the 270–320 nm region is attributed to a $d\sigma \rightarrow d\sigma^*$ transition. It may be attributed to the (Pt–Pt) bond itself, but the system possesses undubitably a substrantial X → Pt charge transfer character according to the dependence of the transition wavelength on X[Cl (270 nm), Br (315 nm)].

Structural Comparisons between Amidate-bridged and Squarato-bridged Tetranuclear Platinum Complexes

Table 2 lists structural features of the two squarato-bridged complexes compared with several tetranuclear amidate-bridged analogues.

It is well known that for one dimensional metal-chain complexes the metal–metal distance is correlated with the formal oxidation state of the metal. Similar relation is also reported for platinum complexes having bridging ligands [26]. Bearing this in mind, the Pt–Pt distances in the squarato bridged

TABLE 1. Infrared Spectral Bands in the Region 1800–1450 cm^{-1} and ν(Pt–X Bands

Compound	ν(C=O)	ν(C=C)	ν(C=C) + ν(C=O)	Pt–X
$[Pt(C_4O_4)(NH_3)_2]_4$ (I)	1798m	1655m	1534, 1501, 1461	
$[Pt(C_4O_4)(NH_3)_2]_2(C_4O_4)_{0.5}\cdot 2H_2O$ (II)	1795m	1655m	1500b	
$[Pt(C_4O_4)(NH_3)_2]_2Cl_2$ (IV)	1800m	1680m	1520b	340
$[Pt(C_4O_4)(NH_3)_2]_2Br_2$ (V)	1800m	1675m	1520b	240

TABLE 2. Comparison of Geometric Features of Amidate-bridged and Squarato-bridged Tetranuclear Platinum Complexes

Compound	Formal Pt oxidation state	Pt–Pt distance (Å)	Pt–Pt–Pt angle (°)	Reference
cis$[(H_3N)_2Pt(C_5H_4NO)_2Pt(NH_3)_2]_2(NO_3)_5 \cdot H_2O$ α-pyridone blue	2.25	2.775 2.877	164.20	6
cis$[(H_3N)_2Pt(C_5H_4NO)_2Pt(NH_3)_2]_2(NO_3)_4$ α-pyridone yellow	2.0	2.992 3.236	160.58	7
cis$[(H_3N)_2Pt(C_4H_5N_2O_2)_2Pt(NH_3)_2]_2(NO_3)_4 \cdot H_2O$ 1-methylhydantoin yellow	2.0	3.131 3.204	160.5	8
cis$[(H_3N)_2Pt(C_4H_6NO)_2Pt(NH_3)_2]_2(NO_3)_6 \cdot 2H_2O$ α-pyridone tan	2.5	2.701 2.710	170.4	26
cis$[(H_3N)_2Pt(C_4O_4)_2Pt(NH_3)_2]_2 \cdot 2H_2O$ (I)	2.0	3.162 3.197	168°	this work
cis$[(H_3N)_2Pt(C_4O_4)_2Pt(NH_3)_2](C_4O_4)_{0.5}$ (II)	2.5	3.05 3.45–3.8		this work

complex **I** are quite long, as expected for a Pt(II) complex. They are similar to those found in the tetranuclear *cis*-diamine platinum 1-methyldantoin yellow (3.13, 3.20) [8] or in other complexes bridged by amides like α-pyridone (2.99, 3.23) [7] where the formal oxidation state of platinum is equal to two.

As already reported, regarding the blue amorphous squarato complex **II**, a tetranuclear model does not fit with the experimental data and the structure of this complex differs largely from that of the amidate-bridged blue compounds. First of all, considering a dinuclear entity the Pt–Pt distance is significantly shorter than that observed in compound **I**. This supports an assignment of an average oxidation state greater than +2. However, this distance (3.05 Å) is notably longer than those observed in amidate-bridged platinum tetranuclear complexes exhibiting the same oxidation state of +2.5 (2.70 Å) [27]. This may be correlated with steric requirements and the rigidness of the squarato ligand which prohibit a shorter Pt–Pt distance. In fact, in the free ligand, the O–O distance is 3.24 Å, and 3.22 Å in complex **I**.

There are also some important differences in the backbone structure of compound **II** compared with classical platinum blues. In platinum blues, we are in occurrence with a zig-zag chain structure limited to four platinum atoms, and in fact, four platinum atoms are requisite to assume delocalization of the single electron associated to the partial oxidation state of 2.25. In squarate blues, only two platinum atoms are able to assume delocalization of the unpaired electron corresponding to the oxidation number of 2.5. One can therefore consider complex **II** as consisting of practically isolated dinuclear entities, the separation between which depends on the preparative batch. This model is compatible with a low solid-state conductivity of $3 \times 10^{-8}\ \Omega^{-1}\ cm^{-1}$, which precludes any electronic delocalization along an infinite chain.

As in the case of amidate platinum blues or binuclear platinum diphosphite complexes [28], oxidative addition to tetranuclear Pt(II) squarate complex is unusually favorable energetically and discrete binuclear Pt(III) complexes are obtained.

Finally, it is worth noting that when the squaric acid is used for synthesis instead of its sodium salt [29], the oxidizing properties of squaric acid become apparent, the resulting complexes being different.

Experimental

Synthesis and Characterization

Products I and II

A mixture of *cis*-diamine platinum(II) hydrolysis products was prepared from 1 mmol of *cis*-$(NH_3)_2$-$PtCl_2$ and 2 mmol of silver nitrate in 10 ml of water. The resulting mixture was left to stand overnight. After removing the silver chloride by centrifugation, the platinum solution was added to an aqueous solution of 2 mmol of squaric acid dissolved in 15 ml of warm water. The mixture then was incubated at 30 °C in the dark to avoid photochemical formation of blue polymers originated from *cis*-diamine platinum(II) hydrolysis products [11]. Upon standing, the solution turned blue. Incubation was stopped after 4 days and an amorphous blue precipitate **II** was removed by filtration. From subsequent reaction of the solution, bright green crystals of **I** were obtained. *Anal.* for the green crystals (**I**): Found: C, 13.04; H, 2.27; N, 7.30; P, 54.55. Calc. for Pt-$(C_4O_4)(NH_3)_2 \cdot H_2O$: C, 13.36; H, 2.22; N, 7.79;

Pt, 54.32%. *Anal.* for the blue compound (**II**): Found: C, 15.20; H, 1.62; N, 7.28; O, 24.35; Pt, 50.58. Calc. for $[Pt(C_4O_4)(NH_3)_2](C_4O_4)_{0.25}\cdot H_2O$: C, 15.50; H, 2.06; N, 7.23; O, 24.8; Pt, 50.38%.

$K_x[Pt(C_4O_4)_2]\cdot 2H_2O$ (III)

This product has been already prepared by Simonsen and Toflund [13] and we have used the preparation scheme described by these authors. *Anal.* Found: C, 18.5; Pt, 37.20; K, 12.8. Calc. for $K_{1.7}[[Pt(C_4O_4)_2]\cdot 2H_2O$: C, 18.41; Pt, 37.40; K, 12.71%.

$X_2[Pt(C_4O_4)_2(NH_3)_2]_2\cdot 2H_2O$, X = Cl (IV), Br (V)

These compounds were prepared by oxidizing compound **I** by nitric acid. A solid sample of compound **I**, 100 mg dissolved in 10 ml of concentrated nitric acid was warmed on a steam bath with stirring until all the compound was dissolved. During this time the solution changed in color to red orange. Then an excess of an aqueous solution of potassium halide (Cl or Br) was added. Subsequent evaporation in air gave red crystals of the compounds. *Anal.* for **IV**. Found: C, 12.28; H, 1.86; N, 7.02; Cl, 8.96; Pt, 48.47. Calc. for $Cl_2[Pt(C_4O_4)(NH_3)_2]_2\cdot 2H_2O$: C, 12.16; H, 2.02; N, 7.09; Cl, 8.99; Pt, 49.42%. *Anal.* for **V**. Found: C, 11.15; H, 12.8; N, 6.19; Br, 18.73; Pt, 45.22. Calc. for $Br_2[Pt(C_4O_4)(NH_3)_2]_2\cdot 2H_2O$: C, 11.16; H, 1.63; N, 6.51; Br, 18.60; Pt, 45.35%.

Physical Measurements

The ESR spectra were recorded on a Brucker ER 200 D spectrometer (X-band, 100 KHz field modulation). The microwave frequency was calibrated with diphenyl picrylhydrazyl. All ESR spectra were recorded on a powdered sample in a large range of temperature.

Magnetic susceptibility was determined by the Faraday method using a Sartorius microbalance coupled with a DRUSH electromagnet. The measurements have been performed between 4 and 320 K. $HgCo(SCN)_4$ was used as standard ($Xg = 10.64 \times 10^{-16}$ μem cgs). The experimental values have been corrected for the diamagnetism of the ligand calculated from Pascal's constants [30]. At several temperatures the magnetic moment was measured as a function of field revealing the presence of an amount of ferromagnetism. Magnetic susceptibility data were corrected for this ferromagnetism extrapolating to infinite field.

All the XPS spectra were obtained with a Vacuum Generators MK1 spectrometer operated in the constant analyzer energy mode (pass energy 20 eV). We used an unmonochromatized Al Kα X-ray source and low X-ray fluxes (power applied to the anode: 45 W) in order to avoid radiation damages. The samples were analyzed in powder shape at ambient temperature under pressures in the 10^{-9} to 10^{-8} mbar range.

The spectrometer was modified to permit data acquisition and treatment [31]. The spectra were summed 9 to 16 times and then smoothed using the binomial filter [32]. The background was subtracted according to Shirley's method [33]. The peak profiles were reconstructed with gaussian-shaped components. Fitting the reconstructed profiles to the experimental ones was performed by computing the difference between the sum of the components and the experimental signal. The intensity ratio of the 4f 7/2 and 4f 5/2 components of the Pt 4f line was close to the 4:3 theoretical expectation. The spectra are internally normalized to the value C_{1s} = 288.5 eV for the carbonyl carbon of the squarate ring.

The infrared spectra of the ligand and complexes were recorded on a Perkin-Elmer Model 577 spectrometer calibrated with polystyrene film using KBr disks.

Reflectance spectra in the UV–Vis range were made on a Cary spectrophotometer.

The compaction conductivity of powdered samples were measured on compressed pellets with a Wayne-Kerr Model B605 Automatic Component bridge.

LAXS Study

The blue compound $Pt(NH_3)_2(C_4O_4)1.25$ was carefully ground and pressed (280 kg/cm^2) into a 0.2–0.3 mm thick pellet and the diffuse spectrum, scattered by the sample irradiated with graphite-monochromatized molybdenum Kα radiation, was obtained using an automatic diffractometer. The pellets were oriented perpendicular to the X-ray beam when the goniometer angles were at zero. About 2000 intensities corresponding to equidistant points were collected in the range $3° < 2\theta < 132°$ (2θ being the diffusion angle) during 24 h. All the measurements were carried out at 22 °C.

All the data processing was carried out on a VAX 11/730 using the LASIP system and have been detailed elsewhere [34]. The scattered intensities were corrected for polarization and absorption effects, normalized by comparison with the sum of coherent and incoherent independent intensities using the methods of Krogh-Moe and Burian *et al.* [35]. The atomic scattering factors for all the atoms were taken from Cromer and Waber [36], and Compton diffusion factors from Cromer [37].

The experimental radial distribution function, $F(r)$ which shows the distribution of the interatomic distances in the polymers, is obtained by using the Zernicke and Prins relation [38]. The theoretical radial distribution function, $F(r)_{theor}$ is calculated for structural models by the Fourier transform of Debye's formula of theoretical intensities [39].

For theoretical calculations interatomic distances in the squarato entities have been deduced from those obtained in the structural determination of compound **I** [16]. All the angles of the ring are assumed to be 90°.

Three samples of compound **III** originated from different batches have been submitted to LAXS analysis.

References

1 K. A. Hofmann and G. Budgge, *Chem. Ber., 41* (1908) 312; R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 2835 (1964).

2 B. Rosenberg, L. Van Camp, J. E. Trosko and V. H. Mansour, *Nature (London), 222*, (1969) 385; B. Rosenberg and L. Van Camp, *Cancer Res., 30* (1970) 1799; P. J. Davidson, P. J. Faber, R. G. Fisher Jr., S. Mansy, H. J. Perisie, B. Rosenberg and L. Van Camp, *Cancer Chemother. Rep., 59* (1975) 287.; N. O. Hill, A. Khan and J. J. King, *Cancer Chemother. Rep., 59* (1975) 647.

3 C. M. Flynn Jr., T. S. Vis Wanathan and R. B. Martin, *Inorg. Nucl. Chem., 39* (1977) 437; B. Lippert, *J. Clin. Hematol. Oncol., 7* (1977) 26; G. Y. H. Chu, R. E. Duncan and R. S. Tobias, *Inorg. Chem., 16* (1977) 2625.

4 J. K. Barton, H. N. Rabinowitz, D. J. Szalda and S. J. Lippard, *J. Am. Chem. Soc., 99* (1977) 2827.

5 J. K. Barton, S. A. Best and S. J. Lippard, *Annals New York, Acad. Sci.*, (1978) 686.

6 J. K. Barton, D. J. Szalda, H. N. Rabinowitz, J. V. Waszezak and S. J. Lippard, *J. Am. Chem. Soc., 101* (1979) 1434; P. Arrizabalaga, P. Castan and J. P. Laurent, *Inorg. Chem., 24* (1985) 3656.

7 L. S. Hollis and S. J. Lippard, *J. Am. Chem. Soc., 103* (1981) 1230.

8 J. P. Laurent, P. Lepage and F. Dahan, *J. Am. Chem. Soc., 104* (1982) 7335.

9 K. Matsumoto and K. Fuwa, *J. Am. Chem. Soc., 104* (1982) 897; K. Matsumoto, H. Takahasi and F. Keiichiro, *J. Am. Chem. Soc., 106* (1984) 2049; K. Matsumoto and K. Fuwa, *Chem. Lett.*, (1984) 569; K. Matsumoto, *Bull. Chem. Soc. Jpn., 58* (1985) 651.

10 T. G. Appleton, R. D. Berry and J. R. Hall, *Inorg. Chim. Acta, 64* (1982) L229.

11 C. Bartocci, C. A. Bignozzi and A. Maldotti, *Inorg. Chim. Acta, 53* (1981) L157.

12 R. Usón, J. Fornies, M. Tomás, B. Menjón, K. Sünkel and R. Bau, *J. Chem. Soc., Chem. Commun.*, (1984) 751.

13 O. Simonsen and H. Toflund, *Inorg. Chem., 20* (1981) 4044.

14 H. Toflund, *J. Chem. Soc., Dalton Trans.*, (1979) 837.

15 T. V. O'Hallaran, M. M. Roberts and S. J. Lippard, *Inorg. Chem., 25* (1987) 957.

16 G. Bernardinelli, P. Castan and R. Soules, *Inorg. Chim. Acta, 120* (1986) 205.

17 C. D. Cook, K. Y. Wan, U. Gelius, K. Hamrin, G. Johanson, E. Olsson, H. Siegbahn, C. Nordling and K. Siegbahn, *J. Am. Chem. Soc., 93* (1971) 1904; W. E. Moddeman, J. R. Blackburn, G. Kumar, K. A. Morgan, R. G. Albridge and M. M. Jones, *Inorg. Chem., 7* (1972) 1715.

18 D. Cahen and J. E. Lester, *Chem. Phys. Lett., 18* (1973) 108; P. Burroughs, A. Hammet, J. F. Mc Gilp and J. Orchard, *J. Chem. Soc., Faraday Trans., 71* (1975) 177; J. M. Bret, P. Castan and J. P. Laurent, *Inorg. Chim. Acta, 51* (1981) 103.

19 P. K. Hascharak, T. D. Williams and S. J. Lippard, *J. Am. Chem. Soc., 106* (1984) 6428.

20 P. Arrizabalaga, P. Castan and J. P. Laurent, *J. Am. Chem. Soc., 106* (1984) 4814.

21 T. V. O'Halloran, P. K. Mascharak, I. D. Williams, M. M. Roberts and S. J. Lippard, *Inorg. Chem., 26* (1987) 1261.

22 P. Kottis and R. Lefebvre, *J. Chem. Phys., 39* (1963) 393.

23 K. W. H. Stevens, *Proc. R. Soc. London, Ser. A 214*, (1952) 237.

24 M. Habenschuss and B. G. Gerstein, *J. Chem. Phys., 61* (1974) 852.

25 J. A. C. Van Ooijen, J. Reedijk and A. L. Spek, *Inorg. Chem., 18* (1979) 1184.

26 T. V. O'Halloran, M. M. Roberts and S. J. Lippard, *Inorg. Chem., 25* (1986) 957.

27 K. Matsumoto, H. Takahashi and K. Fuwa, *Inorg. Chem., 22* (1983) 4086.

28 C. M. Che, F. H. Herbstein, W. P. Schaefer, R. E. Marsh and H. B. Gray, *J. Am. Chem. Soc., 105* (1983) 4604.

29 J. Altman and W. Beck, *Inorg. Chim. Acta, 119* (1986) 203.

30 A. Earnshaw, *Introduction to Magnetochemistry*, Academic Press, New York, 1968.

31 J. C. Fontaine, P. Levoir, M. Delamar, J. J. Meyer and J. L. Paumard, *Anal. Instrum., 16* (1987) 295.

32 P. Marchand and L. Marmet, *Rev. Sci. Instrum., 54* (1983) 1034.

33 D. A. Shirley, *Phys. Rev. B, 5* (1972) 4709.

34 P. Lecante, A. Mosset and J. Galy, *J. Appl. Crystallogr., 18* (1985) 214.

35 Krogh-Moe, *J. Acta Crystallogr., 9* (1956) 951; A. Burian, B. Rzepa, P. Lecante and A. Mosset, *J. Mater. Sci. Lett., 4* (1985) 701.

36 D. T. Cromer and J. T. Waber, *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, 1974.

37 D. T. Cromer, *J. Chem. Phys., 50* (1969) 4857.

38 F. Zernicke and J. A. Prins, *Phys., 41* (1927) 184.

39 P. Debye, *Ann. Phys., Leipzig, 46* (1915) 809.