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Influence of steric and electronic factors in the stabilization of five-coordinate ethylene complexes of platinum(II): X-ray crystal structure of [PtCl₂(2,9-dimethyl-1,10-phenanthroline-5,6-dione)]

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Abstract

Reactions of Zeise's salt (K[Pt(η^2 -C₂H₄)Cl₃]) with oxidized phenanthroline ligands (1,10-phenanthroline-5,6-dione, phedon, and 2,9-dimethyl-1,10-phenanthroline-5,6-dione, Me₂phedon) are reported. Comparison with analogous reactions involving unoxidized phen (1,10-phenanthroline) and Me₂phen (2,9-dimethyl-1,10-phenanthroline) ligands indicates that these latter ligands are less capable to stabilize the five-coordinate species [PtCl₂(η^2 -C₂H₄)(phenanthroline)] in which the phenanthroline and the olefin share the trigonal plane and two chlorines are in the axial positions. The X-ray structure of the four-coordinate species [PtCl₂(Me₂phedon)] indicates that the major difference between oxidized and unoxidized phenanthrolines is the loss of aromaticity of the central ring of phenanthroline. As a consequence, the oxidized phenanthroline becomes more flexible and can undergo a bow-like distortion so to reduce steric interaction between *ortho* substituents of phenanthroline and *cis* chlorine ligands. The increase in stability of the four-coordinate species with Me₂phedon is concomitant with an increase in stability of the five-coordinate precursor complex with ethylene. In the latter case the stabilization is not of sterical origin but stems from reduced electron-donor properties of oxidized phenanthrolines. The balance of the two effects is such that the equilibrium between five- and four-coordinate species is more shifted in favour of the former species in the case of Me₂phedon than in the case of Me₂phen. © 2003 Elsevier B.V. All rights reserved.

Keywords: Platinum; Phenanthroline-dione; Five-coordination; X-ray crystallography

1. Introduction

The reaction between Zeise's salt $(K[PtCl_3(C_2H_4)])$ and bidentate N-donor ligands such as diimines or aliphatic and aromatic diamines (N-N) leads to the formation of five-coordinate complexes having $[PtCl_2(\eta^2$ ethylene)(N-N)] composition and trigonal bipyramidal structure with the two chlorine ligands in the apical positions and the bidentate nitrogen ligand and the ethylene in the equatorial plane [1].

By this procedure a large number of five-coordinate complexes of platinum have been characterized, in quite a few cases also via X-ray analysis [2–7]. The bidentate ligand and the alkene occupy invariably the equatorial plane of the trigonal bipyramid and this spatial disposition is a consequence of two concurrent factors: the good π -acceptor capacity of the unsaturated ligand and the small bite of the chelate ligand. In the equatorial plane are located the three pairs of electrons of the donor ligands and two pairs of non-bonding d electrons of

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platinum, altogether five pairs of electrons, which can be better accommodated if at least one equatorial ligand is a good electron acceptor and the pairs of electrons of the other two donors make a small bite [8].

It was also found that a great bulk of the chelate ligand (particularly when the bulk is located in the ligand plane) stabilizes the five-coordination since the interligand steric interactions are relieved in the trigonal plane of a five-coordinate complex (only three donors) as compared to the square-plane of a four-coordinate species (four donors).

Since five-coordinate species of d^8 transition metals play a fundamental role not only in reactions of ligand substitution and *cis-trans* isomerization, but also in a large variety of catalytic processes (isomerization, polymerization, etc.) [9–11], we considered worth of further investigation the role of the steric and electronic properties of the bidentate ligand upon the stabilization of four- versus five-coordination. Therefore, in the present study, we have extended the investigation to two new bidentate nitrogen ligands: 1,10-phenanthroline-5,6-dione (phedon) and 2,9-dimethyl-1,10-phenanthroline-5,6-dione (Me₂phedon, Scheme 1).

1,10-Phenanthroline-5,6-dione has been extensively used as building block for the synthesis of supramolecular assemblies and metallo-dendrimers because of the two distinct functionalities present in its skeleton: the two diiminic nitrogen atoms in positions 1 and 10 (having high propensity to form chelation compounds) and the *ortho*-quinonoid system on the back positions 5 and 6 (this latter having a reach redox chemistry) [12–15]. A much smaller number of papers has dealt with the analogous ligand bearing methyl substituents in the *ortho* positions (Me₂phedon) probably because the steric bulk limits its coordinating ability [16–19].

In the present paper we report the preparation of four- and five-coordinate platinum(II) complexes with phedon and Me₂phedon and make comparison with the analogous complexes with 1,10-phenanthroline (phen)



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Scheme 1.
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and 2,9-dimethyl-1,10-phenanthroline (Me₂phen). The X-ray structure of the first metal complex with 2,9-dimethyl-1,10-phenanthroline-5,6-dione is also reported.

2. Experimental

2.1. General

Elemental analyses were performed using a Carlo Erba Elemental Analyzer mod. 1106 Instrument. IR Spectra were recorded on Perkin–Elmer Spectrum One and Perkin–Elmer 1600 Series FT-IR spectrophotometers using KBr as solid support for pellets. ¹H NMR spectra were recorded on Bruker Avance DPX-WB 300 MHz and Bruker Avance DRX-WB 400 MHz instruments. Chemical shifts were referred to TMS by using the residual protic peak of the solvent as internal reference [7.23 ppm (¹H) and 77.7 ppm (¹³C) for CDCl₃; 3.30 ppm (¹H) for CD₃OD and 2.05 ppm (¹H) for acetone-d₆].

2.2. Starting materials

Commercial reagent grade chemicals were used without further purification.

 $K[Pt(\eta^2-C_2H_4)Cl_3]$ (Zeise's salt) was prepared according to the method of Chock from potassium tetrachloroplatinate and ethylene gas [20].

1,10-Phenanthroline-5,6-dione (phedon) was prepared according to the procedure reported by Calderazzo et al. [16].

2,9-Dimethyl-1,10-phenanthroline-5,6-dione (Me₂phe*don*) was prepared according to the procedure reported by Garas and Vagg [21] with some modifications. A mixture of 2,9-dimethyl-1,10-phenanthroline (2 g, 8.39 mmol) and potassium bromide (6.8 g, 57.2 mmol) was cooled to -78 °C. Concentrated H₂SO₄ (44 ml) was added dropwise. The temperature was increased to -50 °C and concentrated HNO₃ (24 ml) was slowly added. The thick orange paste was slowly allowed to warm to room temperature and then heated at 90 °C for 16 h. The resulting red solution was poured into deionized water (1500 ml), carefully neutralized with Na₂CO₃, and then extracted with 5×100 ml of CH₂Cl₂. The yellow extracts were washed with water, dried over sodium sulfate, and then the solvent evaporated in vacuo. The orange-yellow solid was recrystallized from methanol (2.1 g, 90% yield). Anal. Calc. for $C_{14}H_{10}N_2O_2$ (FW = 238.25): C, 70.58; H, 4.23; N, 11.76. Found: C, 70.22; H, 4.02; N, 11.17%. ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 8.41 (2H, d, ${}^{3}J_{H-H}$ = 7.97 Hz), 7.45 $(2H, d, {}^{3}J_{H-H} = 7.97 Hz), 2.88 (6H, s). {}^{13}C NMR$ (125.76 MHz, CDCl₃) δ (ppm) = 26.43 (2C, s, C(13)/ C(14); numbering of carbon atoms as reported in Fig. 3), 125.93 (2C, s, C(2)/C(11)), 126.44 (2C, s, C(4)/C(8)), 137.89 (2C, s, C(3)/C(12)), 153.01 (2C, s, C(1)/C(10)), 167.53 (2C, s, C(5)/C(9)), 179.25 (2C, s, C(6)/C(7)). IR (KBr): $v_{max} = 1681$ (C=O), 1578 (C–N) cm⁻¹.

2.3. Preparation of complexes

 $[PtCl_2(\eta^2-C_2H_4)(phedon)]$ (1). This complex was not isolated but only prepared in situ and characterized by NMR spectroscopy. A solution containing 6 mg (0.0155 mmol) of Zeise's salt in deuterated acetone (0.7 ml) cooled at -20 °C was treated with 1,10-phenanthroline-5,6-dione (3.4 mg, 0.0155 mmol) and the resulting solution was immediately transferred into an NMR tube which was inserted in the instrument probe previously refrigerated at -20 °C.

¹H NMR (300.13 MHz, acetone-d₆): δ (ppm) = 9.60 (2H, dd, ${}^{3}J_{\text{H-H}} = 5.20$ Hz, ${}^{4}J_{\text{H-H}} = 1.52$ Hz), 8.80 (2H, dd, ${}^{3}J_{\text{H-H}} = 8.01$ Hz, ${}^{4}J_{\text{H-H}} = 1.52$ Hz), 8.17 (2H, dd, ${}^{4}J_{\text{H-H}} = 8.01$ Hz, ${}^{3}J_{\text{H-H}} = 1.52$ Hz), 4.16 (4H, s with satellites, ${}^{2}J_{\text{Pt-H}} = 64$ Hz).

[*PtCl*₂(*phedon*)] (2). A solution containing 10 mg (0.0258 mmol) of Zeise's salt in CH₃OH (2 ml) was treated with a small excess of 1,10-phenanthroline-5,6dione (6.2 mg, 0.0295 mmol). The resulting solution was kept under stirring at room temperature for 1 h meanwhile a yellow precipitate formed. The precipitate was separated by filtration of the solution, washed with methanol and dried under vacuum. The yield was 93% (11.4 mg). *Anal.* Calc. for [PtCl₂(phedon)] \cdot H₂O, C₁₂H₈Cl₂N₂O₃Pt (FW = 494.18): C, 29.16; H, 1.63; N, 5.67. Found: C, 29.26; H, 1.66; N, 5.67%. IR (KBr): $v_{max} = 1703$ (C=O), 352 (Pt-Cl) cm⁻¹.

 $[PtCl_2(\eta^2-C_2H_4)(Me_2phedon)](3)$. Zeise's salt (50 mg, 0.129 mmol) was dissolved in the minimum amount of methanol and treated with a slight excess of 2,9-dimethyl-1,10-phenanthroline-5,6-dione (37 mg, 0.155 mmol). The resulting yellow solution was kept under stirring at room temperature for 1 h and then left resting for one additional hour meanwhile a yellow micro-crystalline solid separated out. The yellow product was removed from the solution, washed with methanol and dried under vacuum. The mother liquor, left standing for one more day, afforded another crop of compound. This latter was treated as the previous one and the two solids were joint together and analyzed. The overall yield was ca. 66% (48 mg). Anal. Calc. for $[PtCl_2(\eta^2-ethylene)(Me_2phedon)]$, $C_{16}H_{14}Cl_2$ N₂O₂Pt (FW = 532.3): C, 36.10; H, 2.65; N, 5.26. Found: C, 35.94; H, 3.12; N, 4.94%. ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 8.54 (2H, d, ${}^{3}J_{H-H}$ = 8.18 Hz), 7.74 $(2H, d, {}^{3}J_{H-H} = 8.18 \text{ Hz}), 3.69 (4H, s with satellites,$ $^{2}J_{\text{Pt-H}} = 71.32 \text{ Hz}$, 3.39 (6H, s). 13 C NMR (75.48 MHz, CDCl₃): δ (ppm) = 29.05 (2C, s, C(13)/C(14); numbering of carbon atoms as reported in Fig. 3), 39.31 (2C, s, ethylene), 128.22 (2C, s, C(2)/C(11)), 129.28 (2C, s, C(4)/ C(8)), 139.70 (2C, s, C(3)/C(12)), 152.52 (2C, s, C(1)/ C(10)), 168.32 (2C, s, C(5)/C(9)), 176.48 (2C, s, C(6)/

C(7)). IR (KBr): $v_{max} = 1694$ (C=O), 1587 (C=N), and 339 (Pt-Cl) cm⁻¹.

 $[PtCl_2(Me_2phedon)]$ (4). 10 mg (0.0177 mmol) of the five-coordinate complex 3 were dissolved in 3 ml of CHCl₃ and 7 ml of diethyl ether were gently layered on the previous solution in order to have two phases. Orange crystals of complex 4 (6 mg, 67% yield) formed after several days at room temperature: an accurately chosen crystal was analyzed by X-ray spectroscopy. Anal. Calc. for $[PtCl_2(Me_2phedon)] \cdot H_2O$ (the sample, if not kept in dry atmosphere, adsorbs one molecule of water moisture per molecule of complex), $C_{14}H_{12}$ $Cl_2N_2O_3Pt$ (FW = 522.26): C, 32.20; H, 2.32; N, 5.36. Found: C, 32.14; H, 2.21; N, 5.21%. ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 8.61 (2H, d, ${}^{3}J_{H-H} = 8.18$ Hz), 7.71 (2H, d, ${}^{3}J_{H-H} = 8.18$ Hz), 3.57 (6H, s with satellites, ${}^{4}J_{\text{Pt-H}} = 4.10$ Hz). IR (KBr): $v_{\text{max}} = 1699$ (C=O), 1593 (C=N), and 342 and 328 cm⁻¹ (Pt-Cl).

[$PtCl_2(\eta^2-C_2H_4)(Me_2phen)$] (5). This complex was prepared as reported in [4].

2.4. Decomposition of the five-coordinate complexes

A sample containing [PtCl₂(η^2 -C₂H₄)(Me₂phedon)] (3) (2.5 mg, 0.0047 mmol) and [PtCl₂(η^2 -C₂H₄) (Me₂phen)] (5) (2.4 mg, 0.0047 mmol) in CDCl₃ (0.7 ml) was transferred into an NMR tube and ¹H NMR spectra were recorded from time to time leaving the NMR tube at constant temperature (45 °C) in the dark. The amounts of the compounds in solution were evaluated by integration of selected peaks from the spectra.

2.5. X-ray crystallography

2.5.1. Crystal data

C₁₄H₁₀Cl₂N₂O₂Pt, monoclinic, $P2_1/n$, a = 8.9570(2)Å, b = 10.4390(2) Å, c = 15.7160(3), $\beta = 103.3160$ (12)°, V = 1429.97 Å³, Z = 4; F(000) = 944; $D_c = 2.342$ g cm³, $\mu = 101.9$ cm⁻¹. Orange plate-shaped crystals, $0.05 \times 0.22 \times 0.31$ mm³.

2.5.2. Data collection and processing

As many as 8185 reflections (3439 unique) were collected in the range $7.34 \le 2\theta \le 56^{\circ}$, on a Nonius Kappa CD diffractometer equipped with a fine-focus sealed tube graphite-monochromated Mo K α radiation.

Data were corrected for Lorentz and polarization effects, and for absorption effect according to Blessing [22]. Omission of intensities with $I \leq \sigma(I_{obs})$ gave 2797 observed reflections, which were employed for the analysis.

2.5.3. Structure solution and refinement

The structure was solved by Direct Methods application (SIR97) [23] and refined by a full-matrix leastsquares technique (SHELX-L) [24]. Each asymmetric unit contains one independent molecule. All nonhydrogen atoms were refined anisotropically, while hydrogen atoms were placed in idealized positions and had assigned a common isotropic thermal parameter (C–H_{ar} 0.93 Å, C–H_{me} 0.96 Å, U_{iso} (H) = 1.2 U_{iso} (C)). The final cycle of least squares refinement included 193 parameters (weighting scheme applied: $w^{-1} = [\sigma^2(F_o^2) + (0.0908P)^2 + 15.6649P]$, with $P = [(F_o^2 + 2F_c^2)/3]$). The final residuals were R = 0.056, $w_R = 0.135$, while GOF was 1.139. Crystal data and structure refinement are reported in Table 1.

3. Results

The reaction between Zeise's salt (K[PtCl₃(η^2 -C₂H₄)]) and 1,10-phenanthroline-5,6-dione was carried on in deuterated acetone at -20 °C. At this temperature the five-coordinate complex **1** (Scheme 2) is sufficiently stable to allow its characterization by ¹H NMR.

The signal at 9.60 ppm (2H, dd, ${}^{3}J_{H-H} = 5.20$ Hz, ${}^{4}J_{H-H} = 1.52$ Hz) was assigned to protons 2 and 9 (numbering of protons as in Scheme 2). The ca. 0.6 ppm shift at lower field of this signal (the corresponding signal for free phedon falls at 8.98 ppm in CD₃OD) is a clear evidence of N–N coordination of phedon to the metal. The preferential coordination of phedon through the two nitrogen atoms rather than through the *ortho* quinonoid system was also expected on the basis of the greater basicity of the diiminic system with respect to the quinonoid functionality [16,25]. The remaining two signals in the aromatic region of the spectrum, at 8.80 ppm (2H, dd, ${}^{3}J_{H-H} = 8.01$ Hz, ${}^{4}J_{H-H} = 1.52$ Hz) and 8.17 (2H, dd, ${}^{3}J_{H-H} = 8.01$ Hz, ${}^{4}J_{H-H} = 1.52$ Hz), were assigned to protons 4/7 and 3/8, respectively. Finally, the singlet with two satellites at 4.16 ppm (4H, intensity 1:4:1, ${}^{2}J_{H-Pt} = 64$ Hz) was

Table 1 Crystal data and structure refinement for [PtCl₂(Me₂phedon)] (4)

2			
Empirical formula	$C_{14}H_{10}Cl_2N_2O_2Pt \\$		
Formula weight	504.23		
Temperature (K)	293(2)		
Wavelength (Å)	0.71070		
Crystal system	monoclinic		
Space group	$P2_1/n$ (number 14)		
Unit cell dimensions	a = 8.9570(2) Å; $b = 10.4390(2)$ Å;		
	$c = 15.7160(3) \text{ Å } \alpha = 90^{\circ};$		
	$\beta = 103.3160(12)^{\circ}; \gamma = 90^{\circ}$		
Volume (Å ³)	1429.97(5)		
Ζ	4		
Calculated density (Mg/m ³)	2.342		
Absorption coefficient (mm ⁻¹)	10.190		
F(000)	944		
Crystal shape and colour	plate, orange		
Crystal size (mm)	0.05 imes 0.22 imes 0.31		
θ range for data collection	3.67–28.00°		
Reflections collected/unique	8185/3439		
Refinement method	full-matrix least-squares on F^2		
Reflections $[I > 2\sigma(I)]/$	2797/0/193		
restraints/parameters			
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R = 0.056, \ wR = 0.135$		
R indices (all data)	$R = 0.078, \ wR = 0.171$		
Goodness-of-fit on F^2	1.139		



characteristic of a platinum(II) coordinated ethylene in a five-coordinate environment (in four-coordinate platinum(II) complexes the chemical shift is, in the average, 1 ppm at lower field).

The reaction between phedon and Zeise's salt was repeated at room temperature and led to the immediate precipitation of a yellow product (2 in Scheme 2) which was characterized by elemental analysis and IR spectroscopy. The elemental analysis indicated a single phedon ligand per platinum atom as well as two chlorine ligands. The yellow product was totally insoluble in water and methanol as well as in most common organic solvents (with the exception of dimethylsulfoxide and dimethylformamide where decomposition was observed). The coordination of the phedon ligand to platinum through the two iminic nitrogens was supported by the presence, in the IR spectrum, of a sharp band at 1703 cm⁻¹ assigned to the C=O stretching. Such a band is not observed in the reaction products of low-valence organometallic complexes with the quinonoid functionality in which the metal gets oxidized while the quinonoid system is reduced [12,26]. Furthermore, the small shift of this band to high wavenumbers with respect to the free ligand (1686 cm^{-1}) indicates a small increase in the carbonyl bond order consequent to coordination of the two nitrogen atoms to platinum [14,16,26].

Performing the reaction of Zeise's salt with 2,9-dimethyl-1,10-phenanthroline-5,6-dione at room temperature a yellow solid started separating out after ca. 1 h. This product, however, resulted to be the five-coordinate species [PtCl₂(η^2 -C₂H₄)(Me₂phedon)] (3) and not the four-coordinate species obtained under similar experimental conditions in the case of phedon.

The ¹H NMR spectrum of **3** in CDCl₃ (Fig. 1) showed two doublets in the aromatic region at 8.54 (2H, ${}^{3}J_{\text{H-H}} = 8.18$ Hz) and 7.74 ppm (2H, ${}^{3}J_{\text{H-H}} = 8.18$ Hz) assigned to protons 4/7 and 3/8 of Me₂phedon, respectively. The singlet with two satellites at 3.69 ppm (4H, intensity 1:4:1, ${}^{2}J_{H-Pt} = 71.32$ Hz) was assigned to ethylene and showed that the values of chemical shift and coupling constant are very close to those found in the analogous complex with Me₂phen (3.67 ppm and 70 Hz). Finally, the singlet at 3.39 ppm (6H) was assigned to the two methyls of Me₂phedon. The downfield shift of this signal (corresponding signal in the free ligand at 2.88 ppm) is a clear evidence in favour of the N–N coordination of Me₂phedon to the metal [2,4,27]. The coordination of Me₂phedon through the two iminic nitrogens was also confirmed by the presence of a C=O stretching at 1694 cm⁻¹ (very close to those of the free ligand at 1681 cm⁻¹).

The four-coordinate complex 4 was obtained unexpectedly in an attempt of crystallization of 3 from a chloroform/diethylether solution. We discovered afterwards that compound 3 is sensitive to light which greatly accelerates its decomposition to 4.

Complex 4 was found to be almost insoluble in most common solvents, it is only slightly soluble in chloroform where the ¹H NMR spectrum was taken (Fig. 2). Two doublets at 8.61 and 7.71 ppm (each doublet integrates for 2H, ${}^{3}J_{H-H} = 8.18$ Hz) were assigned to the pairs of Me₂phedon protons in position 4/7 and 3/8, respectively.

The singlet with two satellites at 3.57 ppm (6H, ${}^{4}J_{\text{H-Pt}} = 4.10$ Hz) was assigned to the protons of the methyl substituents in positions 2 and 9. The deshielding of the signal belonging to the methyl substituents as well as its small coupling with ¹⁹⁵Pt clearly support N–N coordination of Me₂phedon. Coordination through the nitrogen atoms was also supported by IR evidences such as the C=O stretching band at 1699 cm⁻¹. The squareplanar coordination was also supported by the two bands at 342 and 329 cm⁻¹ assigned to the symmetric



Fig. 1. ¹H NMR spectrum (300 MHz) of complex [PtCl₂(η^2 -C₂H₄)(Me₂phedon)] (3) in CDCl₃ (the asterisk indicates the solvent peak).



Fig. 2. ¹H NMR spectrum (300 MHz) of [PtCl₂(Me₂phedon)] (4) in CDCl₃ (the asterisk indicates the solvent peak flanked by weak side bands caused by coupling with 13 C).

and antisymmetric Pt–Cl stretchings stemming from the two chloro ligands coordinated in *cis* position.

It is worth noting the greater downfield shift (0.18 ppm) of the methyl substituents in the positions 2 and 9 observed in the four-coordinate complex 4 as compared to the five-coordinate species 3. This feature is indicative of a stronger ligand-metal ion interaction in 4 than in 3. We have already pointed out that in the trigonal plane of a trigonal bipyramidal platinum(II) species insist five pairs of electrons, three from the three donors and two from non-bonding d-orbitals of the metal. Therefore metal-ligand bonds in the trigonal plane will be basically weaker than those formed in square-planar four-coordinate compounds.

4. Crystal structure

A view of the structure of complex 4, together with the atomic numbering scheme, is given in Fig. 3, fractional atomic coordinates are given in Table 2. There are no atoms in special position. The Pt atom shows square planar coordination, with two nitrogen and two chlorine atoms in *cis* positions; it is evident a pyramidal distortion with the platinum atom displaced by 0.17 Å from the mean plane defined by the four donors, the latter atoms are coplanar within ± 0.03 Å. The N(1)–Pt–N(2) angle of $79.6(3)^{\circ}$ is largely determined by geometrical constrains inside the chelate ring, while the deviation from ideality (90°) of other angles between *cis*-ligands is mainly due to interligand steric interactions (see Table 2). In particular the close contacts between chlorine atoms and contiguous Me groups $[Cl(1) \cdot \cdot \cdot C(14) = 3.24(1) \text{ and}$ $Cl(2) \cdots C(13) = 3.27(1)$ Å and, correspondingly, $Cl(1) \cdots$ H(143) = 2.73 and $Cl(2) \cdots H(133) = 2.46$ Å; sum of the Cl and H van der Waals radii = 2.95 Å] [28] determine considerable distortions within the phenanthroline ligand and within the coordination sphere (Fig. 3, bottom view).

Within the phenanthroline ligand relevant distortions are: (i) a bending of the phenanthroline plane, which assumes a bowlike conformation with a dihedral angle between the mean planes through the external rings [N(1)-C(1)-C(2)-C(3)-C(4)-C(5)]and N(2)-C(10)-C(11)-C(12)-C(8)-C(9)] of 22.7(4)° [16.6(4)° in the analogous complex with Me₂phen]; (ii) a remarkable rotation of the ligand plane around the N(1)-N(2) vector so that the chelating moiety [N(1)-C(5)-C(9)-N(2)]forms with the coordination plane [N(1)-Pt-N(2)] a dihedral angle of $29.5(5)^{\circ}$ [27.5(5)° in the complex with Me₂phen]; (iii) a displacement of the methyls from the phenanthroline plane as indicated by the torsion angles Me–C–N–C of 13.6° and 16.5° (14.0° and 10.2° in the case of Me₂phen).

Within the coordination sphere most relevant distortions are: (i) a narrowing of the Cl-Pt-Cl angle to



Fig. 3. View of the asymmetric unit of $[PtCl_2(Me_2phedon)]$ (4) with the atomic numbering scheme. Ellipsoids are drawn at 50% probability. Above is shown the top view and below the front view.

86.8(1)° [85.8(1)° for Me₂phen]; (ii) a widening of the Cl–Pt–N angles to $97.7(3)^{\circ}$ and $94.3(3)^{\circ}$ [97.8(3)° and $95.4(3)^{\circ}$ in the case of Me₂phen].

Oxygen atoms O(1) and O(2) and carbon atoms C(6) and C(7) show sp² hybridization, with C=O double bond lengths of 1.218(14) and 1.199(15) Å, respectively, in good agreement with literature values [16,29,30]. The presence of C=O bonds determines the loss of aromaticity of the central ring, with respect to the external ones, as indicated by the lengthening of the C–C bonds which, with the only exception of the C(4)–C(5) and C(8)–C(9) bonds shared with the external rings, are, on the average, 0.11 Å longer. The same bonds are, on the average, 0.09 Å longer in 4 than in the corresponding compound with Me₂phen [31,32]. Particularly indicative is the C(6)–C(7) distance which results to be 1.52 Å in the present case, while it was 1.34 Å in the case of Me₂phen.

Table 2 Bond distances (\mathring{A}) and angles (°) for [PtCl₂(Me₂phedon)] (4)

Bond distances		Bond angles		
Pt(1)–N(1)	2.028(10)	N(1)–Pt–N(2)	79.6(3)	
Pt(1)–N(2)	2.032(8)	Cl(1)-Pt-Cl(2)	86.81(15)	
Pt(1)-Cl(1)	2.302(3)	Cl(1)-Pt-N(2)	94.3(3)	
Pt(1)-Cl(2)	2.290(3)	Cl(2)-Pt-N(1)	97.7(3)	
O(1)–C(7)	1.218(14)	Pt-N(1)-C(1)	132.2(9)	
O(2)–C(6)	1.199(15)	Pt-N(1)-C(5)	110.4(7)	
N(1)–C(1)	1.366(14)	C(1)–N(1)–C(5)	116.7(10)	
C(1)–C(2)	1.39(2)	N(1)-C(1)-C(13)	119.3(12)	
C(2)–C(3)	1.37(2)	N(1)-C(1)-C(2)	119.6(12)	
C(3)–C(4)	1.399(19)	C(2)-C(1)-C(13)	120.9(12)	
C(4)–C(5)	1.358(16)	C(1)-C(2)-C(3)	122.2(12)	
C(5)–N(1)	1.349(14)	C(2)–C(3)–C(4)	117.9(13)	
C(4)–C(6)	1.495(19)	C(3)-C(4)-C(5)	117.2(13)	
C(5)–C(9)	1.495(14)	C(3)-C(4)-C(6)	121.8(12)	
C(1)–C(13)	1.488(19)	C(5)-C(4)-C(6)	120.9(11)	
N(2)–C(10)	1.360(14)	C(4)-C(5)-N(1)	125.7(10)	
C(10)–C(11)	1.391(17)	C(9)-C(5)-N(1)	113.2(9)	
C(11)–C(12)	1.380(19)	C(4)–C(5)–C(9)	121.0(10)	
C(8)–C(12)	1.387(18)	C(4)–C(6)–C(7)	117.9(10)	
C(8)–C(9)	1.394(15)	Pt-N(2)-C(10)	130.7(7)	
C(9)–N(2)	1.321(14)	Pt-N(2)-C(9)	109.7(7)	
C(7)–C(8)	1.487(17)	C(9)-N(2)-C(10)	119.5(9)	
C(6)–C(7)	1.519(19)	N(2)-C(10)-C(14)	120.0(10)	
C(10)–C(14)	1.493(17)	N(2)-C(10)-C(11)	118.8(11)	
		C(11)-C(10)-C(14)	121.1(11)	
		C(10)-C(11)-C(12)	120.8(11)	
		C(11)–C(12)–C(8)	119.0(11)	
		C(12)-C(8)-C(9)	117.1(11)	
		C(12)–C(8)–C(7)	122.7(10)	
		C(9)–C(8)–C(7)	120.2(11)	
		C(8)-C(9)-N(2)	123.2(10)	
		C(5)–C(9)–N(2)	115.7(9)	
		C(8)–C(9)–C(5)	120.6(10)	
		C(8)–C(7)–C(6)	117.5(10)	
		O(1)–C(7)–C(8)	121.7(12)	
		O(1)–C(7)–C(6)	120.9(12)	
		O(2)–C(6)–C(4)	122.4(13)	
		O(2)–C(6)–C(7)	119.8(13)	

Two interesting observations stem from comparison between the X-ray data of compound 4 and the analogous compound with Me₂phen, these are: (i) distortions within the phenanthroline ligand generally greater for Me₂phedon than for Me₂phen and (ii) distortions within the coordination sphere generally smaller for Me₂phedon than for Me₂phen. Both features originate from the loss of aromaticity of the central ring of Me₂phedon which renders the ligand slightly more flexible and, as a consequence, more adaptable to the requirements of the coordination sphere which, therefore, becomes slightly less distorted.

5. Crystal packing

The three-dimensional array is made of pairs of quasi parallel [PtCl₂(Me₂phedon)] moieties. Within each pair the two molecules are rotated by 180° , one with respect

to the other, so that the chlorine atoms of one subunit interact with the phenanthroline of the other subunit [shortest distances $Cl(1) \cdots C(6) = 3.14(1)$ Å, $Cl(1) \cdots$ C(7) = 3.12(1) Å, $Cl(2) \cdots C(7) = 3.21(1)$ Å, and $Cl(2) \cdots$ C(8) = 3.33(1) Å] (Fig. 4). Adjacent pairs are quasi orthogonal to each other so that each phenanthroline has, on one side, the chlorine atoms of the second subunit and, on the other side, the chlorine atoms of a neighbouring pair.

The three-dimensional array is also stabilized by strong electrostatic interactions between protons of methyl C(14) and oxygen atom O(1) $[O(1)\cdots H(143)(x+1/2, -y+1/2, z+1/2) = 2.65(1)$ Å and O(1) \cdots H(142)(-x + 1/2, y - 1/2, -z + 1/2) = 2.87(1) Å], between aromatic proton H(11) and oxygen atom O(1) $[O(1)\cdots H(11)(-x + 1/2, y - 1/2, -z + 1/2) = 2.49(1)$ Å], and between aromatic proton H(12) and chlorine ligand Cl(2) $[Cl(2)\cdots H(12)(x+1/2, -y + 1/2, z - 1/2) = 2.85(1)$ Å].



Fig. 4. Crystal packing of [PtCl₂(Me₂phedon)] (4) down the a axis.

6. Discussion and conclusion

Two different types of coordination compounds are expected from a d⁸ metal ion like platinum(II): fourcoordinate square-planar and five-coordinate trigonal bipyramidal (or square pyramidal) species. Although complexes of the second type are coordinatively saturated, they are much less common than four-coordinate complexes which, instead, have an unsaturated coordination shell [2]. The common procedure for the preparation of a five-coordinate complex from a four-coordinate precursor is the substitution of a bidentate ligand (usually a N-donor ligand with a small bite) for a monodentate ligand in the starting substrate. This synthetic pathway was used by Maresca et al. [1] for the preparation of the five-coordinate complex with phen. Starting with Zeise's salt and free ligand in methanol and performing the reaction at 0 °C, the five-coordinate complex $[PtCl_2(\eta^2 C_2H_4$)(1,10-phenanthroline)] was obtained as a crystalline solid. In solution in common organic solvents the compound tends to decompose releasing ethylene and affording the corresponding square-planar complex $[PtCl_2(1,10-phenanthroline)]$. The decomposition can be repressed by keeping the solution at low temperature (below -10 °C).

The same trend was observed by us using the phedon ligand instead of phen. At -20 °C we were able to obtain and characterize the five-coordinate complex [PtCl₂(η^2 -C₂H₄)(phedon)] (1) which resulted to be stable at that temperature. On the other hand, when we repeated the reaction at room temperature we obtained the precipitation of the four-coordinate complex [PtCl₂(phedon)]

(2), exactly as in the case of phen. Compound 2, as the analogous complex with phen, resulted to be insoluble in most common organic solvents preventing the investigation of the dissociation equilibrium:

$$[PtCl_2(\eta^2 - C_2H_4)(N-N)] \rightleftharpoons [PtCl_2(N-N)] + C_2H_4 \quad (1)$$

If 2,9-dimethyl-1,10-phenanthroline (Me₂phen) is used instead of phenanthroline, the five-coordinate complex, [PtCl₂(η^2 -C₂H₄)(Me₂phen)], is much more stable even at ambient temperature [4,33]. The steric hindrance of the methyl substituents stabilizes the fivecoordinate species which places the Me₂phen ligand in the equatorial plane in which insist only three donor groups.

The reaction between Zeise's salt and the Me₂phedon also afforded the five-coordinate complex **3** as a stable species. In order to study the effect of the electronattracting *ortho*-quinonoid system upon the stabilization of the five-coordinate species, we investigated the decomposition equilibrium (1) in a NMR sample containing both [PtCl₂(η^2 -C₂H₄)(Me₂phedon)] (**3**) and [PtCl₂(η^2 -C₂H₄)(Me₂phen)] (**5**). The percentages of different species, as a function of time, are reported in Fig. 5. At equilibrium only ca. 20% of complex **3** had decomposed to **4**, while decomposition was ca. 60% for complex **5**.

The greater stability of the five-coordinate complex with Me_2 phedon, as compared to the analogous complex with Me_2 phen, stems from reduced electron-donor capacity of the oxidized phenanthroline which helps in diminishing the electron charge accumulation in the trigonal plane of the five-coordinate species.

Moreover such a stabilization could be greater than what appears from the shift in the equilibrium between



Fig. 5. Relative percentages of the five-coordinate complexes $[PtCl_2(\eta^2-C_2H_4)(Me_2phedon)]$ (3) and $[PtCl_2(\eta^2-C_2H_4)(Me_2phen)]$ (5) and the four-coordinate complexes $[PtCl_2(Me_2phedon)]$ (4) and $[PtCl_2(Me_2phen)]$ (6) plotted as a function of time. Values calculated from integration of selected peaks from the NMR spectra.

five- and four-coordinate species if the Me_2 phedon ligand destabilizes the four-coordinate species less than Me_2 phen. The latter hypothesis is supported by the X-ray investigation showing how the interligand steric interactions are somewhat less severe in the fourcoordinate complex with Me_2 phedon than in the complex with Me_2 phen.

Therefore this investigation gives a further proof of the crucial role played by the electron-charge accumulation in the equatorial plane of the trigonal bipyramid on the stability of five-coordinate d^8 metal complexes. In addition to the π -acceptor ability of equatorial ligands such as olefines and acetylenes, extensively investigated in the past, also a reduced electron-donor capacity of the other equatorial ligands, generally a diamine, can stabilize the five-coordinate species.

7. Supplementary materials

Full crystallographic data for the reported complexes have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 211482. Copy may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http:// www.ccdc.cam.ac.uk).

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