Chiroptical Properties of Diastereomeric Five-coordinate Pt(II)–Olefin Complexes. Molecular Structure of $[PtCl_2\{(S,S)\text{-}(E)\text{-}CNCH{=}CHCN\}(R,R)\text{-}\{C_6H_5CH(CH_3)N(CH_3)CH_2\}_2]\cdot C_6H_6$

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Abstract

The chiroptical properties of five-coordinate diastereomeric complexes of general formula $[PtCl_2(R,R)\text{-}\{C_6H_5CH(CH_3)N(CH_3)CH_2\}_2\{olefin\}]$, with olefin ligands having electron-withdrawing substituents, have been investigated. The sign of CD bands in the 28 000–30 000 cm^{-1} region appears to be correlated to the absolute configuration of the prochiral coordinated alkene. Single-crystal X-ray diffraction structure determination has been performed on the single diastereomer $[PtCl_2(E\text{-but-2-enedinitrile})(R,R)\text{-}\{C_6H_5CH(CH_3)N(CH_3)CH_2\}_2]\cdot C_6H_6$. The compound crystallizes in the monoclinic space group C2 with $a = 17.842(2)$, $b = 8.466(1)$, $c = 10.464(1)$ Å, $\beta = 109.34(1)°$, $Z = 2$. The number of observed reflections was 1943 and the final R and R_w values were 0.020 and 0.028 respectively. Trigonal-bipyramidal geometry is observed around the Pt atom, with the two Cl atoms in axial positions. The unsaturated ligand lies in the equatorial plane disclosing S,S absolute configuration.

Introduction

In a recent paper [1] on the chiroptical properties of five-coordinate olefin complexes of platinum(II), we examined the 20 000–40 000 cm^{-1} CD spectra of several enantiomeric compounds of general formula [PtCl$_2$(N-N)(olefin)], where (N-N) is a bidentate nitrogen ligand and olefin stands for a chiral or a prochiral alkene. When the olefin is an ethylene homologue, the comparison of these spectra with those of square-planar olefin–platinum(II) complexes shows that the quadrant rule [2], which links the absolute configuration of the coordinated alkene to the sign of the lower field CD band, does not hold in case of trigonal-bipyramidal geometry. However, all the examined compounds show in the 28 000–30 000 cm^{-1} region an absorption maximum of medium to high intensity which, if positive, can be assumed diagnostic of the R configuration for the coordinated unsaturated ligand.

When the coordinated olefin is an alkene with electron-withdrawing substituents, a similar intense band was observed [1] in the 28 000–30 000 cm^{-1} region. No correlation between absolute configuration and sign of this band was proposed, since configurational assignments by X-ray analysis were not available and reference could not be made to corresponding square-planar compounds.

In this paper we report a study on the chiroptical properties of diastereomeric [PtCl$_2$(R,R-diam)(olefin)] complexes where the olefin bears electron-withdrawing substituents groups and R,R-diam is $R,R\text{-}\{C_6H_5CH(CH_3)N(CH_3)CH_2\}_2$. The crystal structure of a single diastereoisomer [PtCl$_2$(E-but-2-enedinitrile)(R,R-diam)] is also presented looking for a correlation between absolute configuration and CD spectra.

Results and Discussion

Optically active [PtCl$_2$(R,R-diam)(olefin)] complexes, with olefin = E-CNCH=CHCN (FDN); $CH_2{=}CHCN$ (ACN); $CH_2{=}CHCHO$ (ACA); and $CH_2{=}CHCOOMe$ (ACM) were prepared, following a known procedure [3], by olefin exchange in benzene solution starting from the corresponding ethylene complex

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$$[PtCl_2(C_2H_4)(R,R\text{-diam})] + \text{olefin} \rightleftharpoons [PtCl_2(R,R\text{-diam})(\text{olefin})] + C_2H_4$$

A distinct asymmetric induction is observed with regard to the coordination of the alkene to the metal centre. In particular, the complex containing FDN crystallizes from the reaction medium quantitatively in the form of a single diastereoisomer as suggested by the ^{1}H NMR spectra [3] and ultimately confirmed by X-ray structural analysis (*vide infra*). In addition no epimerization is observed in solution. A different behaviour is shown by the complex containing ACN. In fact the ^{1}H NMR spectrum of the recrystallized compound is, as already observed [3], time-dependent. The spectrum, recorded within 3 min from the dissolution, indicates a diastereoisomeric mixture of approximate composition 4:1 which changes after 30 min until a slight prevalence of the diastereoisomer which is less abundant after the dissolution. Facing these remarkable spectral variations, the optical activity of the compound moderately changes from $[\alpha]_D^{20} = +103°$ (2 min after the dissolution) to $[\alpha]_D^{20} = +89°$ (after 30 min). A simple rationalization can be found assuming that the molar contribution to the optical activity of the compound from the coordinated ACN be a half of that assignable to FDN. On these grounds the optical activity of the two diastereoisomeric pure forms should differ only by ±20° from the value corresponding to a 1:1 mixture. In addition, the comparison of the optical values should indicate that the coordinated ACN in the recrystallized solid complex has absolute configuration opposite to that of FDN. These conclusions necessarily imply the configuration of the two N atoms of the *R,R*-diam being the same as in ethylene, FDN and ACN complexes. Actually no evidence of configurational variations regarding the coordinated *R,R*-diam after the olefin exchange reactions was ever observed. We note that configuration retention is clearly proved at least in the case of the FDN complex (see Table I).

TABLE I. Optical Data for $[PtCl_2(R,R\text{-diam})(\text{olefin})]$ Complexes

Olefin in the complex	$[\alpha]_D^{20}$	$[M]_D$
Ethylene	+99	580
FDN	+43^a	340
ACN	+103 (t = 2′)	630
	+89 (t = 30′)	550
ACA	−75	−460
ACM	+116	750

^{a}Value for a crystallized complex containing one C_6H_6 molecule.

With reference to ACA and ACM containing complexes, in both cases the ^{1}H NMR spectra are consistent [3] with the presence in solution of a single, or a largely predominant diastereoisomer, and no variations of the spectral pattern are observed with time. The presence of different substituents on the coordinated double bond does not allow simple comparison with the optical properties of the FDN and ACN complexes. However it is worth noting the very high molar contribution to the optical activity from the coordinated ACA. In fact, in some preparations we obtained crude products with optical activities markedly lower than the reported value, without significant differences in the ^{1}H NMR spectra. In these cases, however, the limit value of $[\alpha]_D^{20} = -75°$ is attained by recrystallization or by a fast anti-epimerization in solution.

The CD spectra of the previous complexes have been recorded in chloroform solution and are reported in Fig. 1 (ethene, FDN and ACN complexes) and Fig. 2 (ACA and ACM complexes). The absorption pattern of the ACN complex refers to a spectrum recorded as rapidly as possible immediately after the dissolution of the sample.

By comparison of the spectral data, it can be seen that the lower field region until *ca.* 26000 cm^{-1} is not particularly sensitive to the presence of the chiral coordinated unsaturated ligand since there are no significant differences with respect to

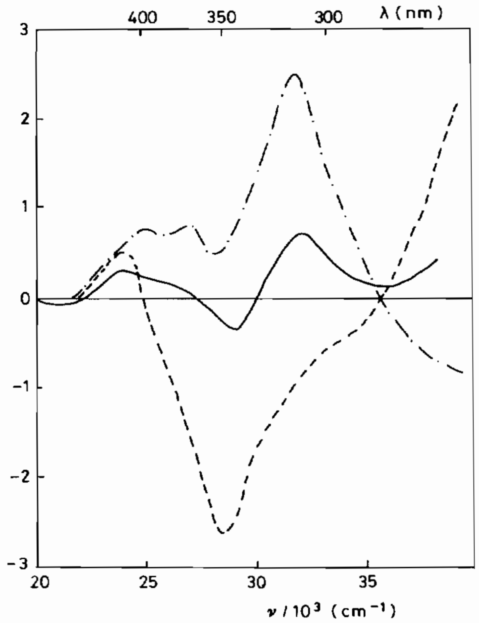

Fig. 1. CD spectra, in chloroform solution of the $[PtCl_2(R,R\text{-diam})(\text{olefin})]$ complexes. Solid line, ethylene complex; broken line, FDN complex; broken line with dots, ACN complex (spectrum recorded immediately after dissolution of the sample).

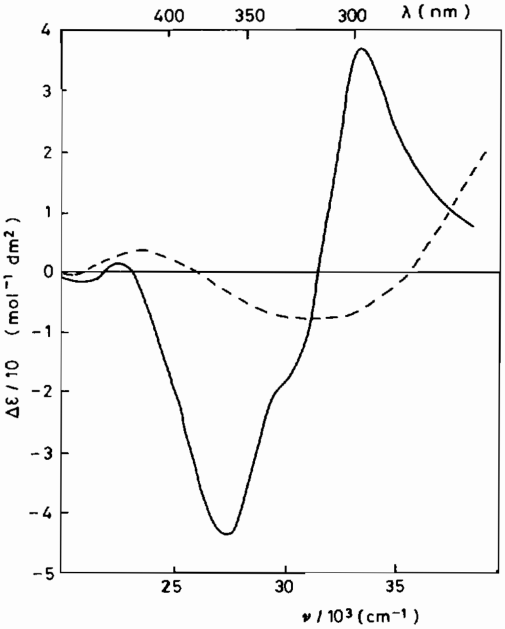

Fig. 2. CD spectra, in chloroform solution of the [$PtCl_2$-(*R,R*-diam)(olefin)] complexes. Solid line, ACA complex; broken line, ACM complex.

the ethylene complex. On the other hand strong absorption bands are observed in the 28 000–30 000 cm^{-1} region. In particular the FDN complex shows a maximum centered at 28 500 cm^{-1} with $\Delta\epsilon = -26.5$ mol^{-1} dm^2. In the case of the ACN complex (see Fig. 1), the analysis of the CD spectrum in this region is complicated owing to the variation of the diastereomeric composition with time attaining negative and constant values after half an hour. Assuming this absorption is related to the absolute configuration of the chiral alkene, the coordinated ACN should have a configuration opposite to that presented by FDN, as already argued by the analysis of the optical activities. It must be noted that the reported [1] enantiomeric complexes (–)[$PtCl_2$-(FDN)(BBDH)] and (+)[$PtCl_2$(ACN)(BBDH)] (BBDH = 2,3-butandione-bis-*N,N*-dimethylhydrazone) obtained by (N-N) exchange from the corresponding *R,R*-diam complexes show negative and, respectively, positive dichroism at *ca.* 29 000 cm^{-1}.

In Fig. 2 CD spectra of ACA and ACM complexes are reported and in both cases negative absorption bands are visible in the 28 000–30 000 cm^{-1} region, as observed [1] for the corresponding enantiomeric BBDH complexes.

The X-ray structural determination performed on the diastereomeric [$PtCl_2$(*R,R*-diam)(FDN)] complex (*vide infra*) discloses an *S,S* absolute configuration of the coordinated alkene.

Therefore, we suggest that, as in already reported five-coordinate complexes with ethylene homologues, positive dichroism in the 28 000–30 000 cm^{-1} region is diagnostic of an *R* configuration of the Pt(II)-coordinated alkene in a tbp geometry.

We wish to note that in another case of tbp geometry, such as (–)[$Fe(CO)_4$(*R,R*-fumaric acid)], a positive maximum is found [4] at 27 800 cm^{-1}. Other studies with different metals are in progress to ascertain the influence of the coordination centre.

Molecular Structure of [$PtCl_2$(R,R-diam)(FDN)] • C_6H_6

Crystals of the title compound consist of discrete monomeric molecules lying around a crystallographic C_2 axis and clathrated benzene molecules slightly disordered about a site of C_2 symmetry. The ratio between the complex and solvent molecules is 1/1.

Two views of the molecule are shown in Figs. 3 and 4.

Selected bond distances and angles of the structure model are reported in Table II. The symmetry axis of the complex molecule contains the Pt atom and passes through the midpoints of the C(1)–C(1)′ and C(2)–C(2)′ bonds. The Pt atom displays five-coordination with trigonal-bipyramidal geometry. The two chloride ligands occupy the axial positions while the equatorial coordination sites are occupied by two nitrogen atoms of the chelating *R,R*-diam ligand and by the π bonded fumarodinitrile carbon atoms C(2) and C(2)′.

TABLE II. Selected Molecular Parameters[a]

(a) Bond Distances (Å) and Angles (°)			
Pt–Cl	2.314(1)	Pt–N(1)	2.287(4)
Pt–C(2)	2.073(5)	N(1)–C(1)	1.470(7)
C(1)–C(1)′	1.539(9)	N(1)–C(11)	1.542(6)
N(1)–C(1)M	1.497(8)	C(11)–C(2)M	1.520(8)
C(11)–C(111)	1.505(10)	C(2)–C(2)′	1.480(12)
C(2)–C(3)	1.452(8)	C(3)–N(4)	1.131(9)
Cl–Pt–Cl′	175.2(3)	N(1)–Pt–N(1)′	81.2(2)
C(2)–Pt–C(2)′	41.8(3)	N(1)–Pt–C(2)	118.6(3)
Pt–N(1)–C(1)	103.5(3)	N(1)–C(1)–C(1)′	110.7(4)
Pt–N(1)–C(11)	113.9(3)	C(1)–N(1)–C(1)M	109.8(5)
C(1)M–N(1)–C(11)	109.0(4)	Pt–N(1)–C(1)M	112.2(3)
C(1)–N(1)–C(11)	108.2(4)	N(1)–C(11)–C(111)	112.2(5)
C(2)M–C(11)–C(111)	114.7(5)	N(1)–C(11)–C(2)M	110.7(5)
C(2)′–C(2)–C(3)	119.9(6)	C(2)–C(3)–N(4)	175.2(7)
Pt–C(2)–C(2)′	69.1(2)	Pt–C(2)–C(3)	117.5(4)
(b) Torsional Angles (°)			
Pt–N(1)–C(1)–C(1)′	44.7(4)		
N(1)–C(1)–C(1)′–N(1)′	-65.4(4)		
C(3)–C(2)–C(2)′–C(3)′	40.0(4)		
N(1)–Pt–C(2)–C(3)	62.1(5)		
C(2)–Pt–N(1)–C(11)	44.9(4)		
Pt–N(1)–C(11)–C(111)	168.0(4)		

[a] e.s.d.s given in parentheses.

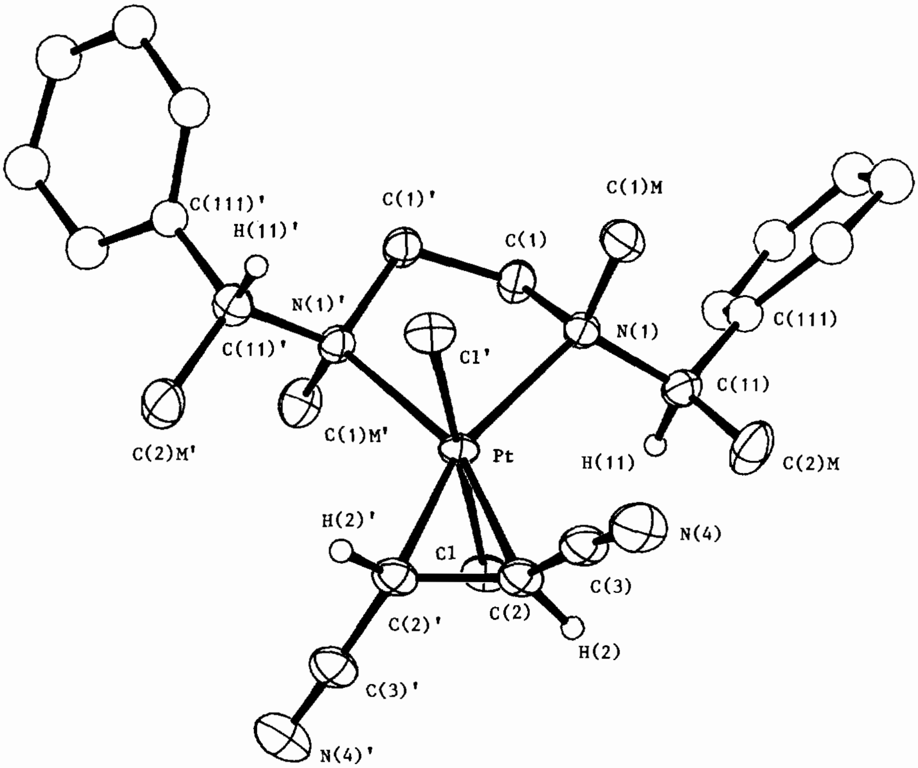

Fig. 3. ORTEP drawing of the [$PtCl_2$(*E*-but-2-enedinitrile)(*R,R*-diam)] molecule. Thermal ellipsoids are drawn at 30% probability.

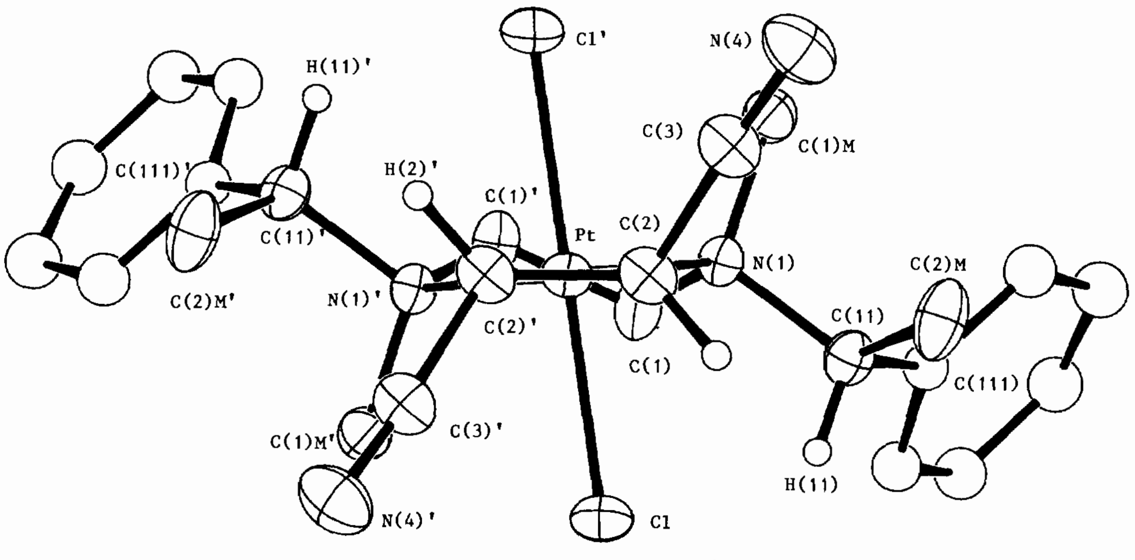

Fig. 4. Projection of the [$PtCl_2$(*E*-but-2-enedinitrile)(*R,R*-diam)] molecule down the C_2 axis.

The substituted ethylenediamine ligand contains two pairs of chiral atoms, *i.e.* C(11), N(1) and their symmetry equivalents C(11)', N(1)'. C(11) and C(11)' have predetermined absolute configuration *R*, while N(1) and N(1)', that in the free ligand are considered prochiral, are frozen in *R* configuration upon coordination to platinum. The diastereoisomer with *R* configuration at all the chiral centres appears to be the one that optimizes the contacts between the most hindering substituents at the nitrogen atoms, *i.e.* $PtCl_2$ and C(Ph)(Me)H. The lack of other isomers in the reaction mixture is indicative of complete induction of the carbon atoms chirality on that of the nitrogen atoms. The chelated ligand exhibits conformational chirality due to the puckering of the five-membered ring. As one can appreciate in Fig. 3, the ring conformation is λ, according to the Hawkins–Larsen notation [5]. Such a conformation seems dictated by the need of putting the most hindering ring substituents, the C(Ph)(Me)H groups, in equatorial positions. The ring conformation is therefore induced by the nitrogen atoms configuration. These considerations are completely consistent with those found [3] for the same ligand in $[PtCl_2(C_2H_4)(R,R\text{-diam})]$ and $[PtCl_2(MeCH{=}CH_2)(R,R\text{-diam})]$.

The Cl–Pt–Cl′ linkage (Pt–Cl 2.314(1) Å) is slightly bent toward the fumarodinitrile ligand (175.2(3)°), and is not perpendicular to the best plane defined by the equatorial atoms Pt, N(1), N(1)′, C(2), C(2)′. An inspection of the intramolecular contacts of the chlorine atoms shows that this arrangement is required in order to preserve normal van der Waals interactions with the methyl hydrogens of C(1)M (Cl...HC(1)M 2.66 Å), and is made possible by the favourable conformation of the C(Ph)(Me)H group which points its least hindering atom H(11) towards Cl (Cl...H(11) 2.64 Å). The value of 2.287(4) Å for the Pt–N(1) bond is significantly shorter than the corresponding interactions of the same ligand in $[PtCl_2(C_2H_4)(R,R\text{-diam})]$ 2.372(12) Å and in $[PtCl_2(MeCH{=}CH_2)(R,R\text{-diam})]$ 2.354(9) Å. This shortening is probably an effect of a greater electron density removal from the Pt atom brought about by the fumarodinitrile ligand. The same distance is as expected slightly longer than those found in other five-coordinate species closely related to the present one, where the ligand nitrogen atoms possess sp^2 hybridization [6]. Other bonding parameters within the *R,R*-diam are normal.

The way in which the prochiral fumarodinitrile coordinates to platinum and the resulting absolute configuration *S* of atoms C(2) and C(2)′ are strictly related to the coordination stereochemistry of the $\{PtCl_2(R,R\text{-diam})\}$ fragment. A calculated model in which the olefinic ligand is coordinated to the metal through the opposite enantioface shows too short contacts between –C≡N and C(2)M methyl groups. The Pt–C(2) distance, 2.073(5) Å, can be compared to the corresponding interactions in (+)$[PtCl_2(E\text{-2-butene})$(2,3-butanedionebis-*N,N*-dimethylhydrazone)], average 2.075 Å [6]. The coordination of the fumarodinitrile ligand results in a lengthening of the C=C bond (C(2)–C(2)′ 1.48(1) Å) with respect to the uncoordinated double bond (see for instance the value of 1.350(4) Å in dichlorofumarodinitrile [7] and that of 1.36 Å in tetracyanoethylene [8]), and in a bending away from the Pt atom of the –C≡N appendages, the torsional angle C(3)–C(2)–C(2)′–C(3)′ being 40.0(4)°. The C(2)–C(3)–N(4) system slightly deviates from linearity probably because of packing effects (C(2)–C(3)–N(4) = 175.2(3)°). The C(2)–C(3) and C(3)–N(4) distances compare well with the corresponding ones in dichlorofumarodinitrile and tetracyanoethylene.

Experimental

Solvents and reagents were of AnalaR grade. ^1H NMR spectra were recorded on a Bruker WH 270 MHz spectrometer; $CDCl_3$ was used as solvent and tetramethylsilane as internal reference. Optical activities were determined on a Perkin-Elmer 141 polarimeter. The CD spectra were obtained on a JASCO J500-A spectropolarimeter.

Platinum Complexes

The $[PtCl_2(R,R\text{-diam})(\text{olefin})]$ complexes (olefin = ethylene, *E*-but-2-enedinitrile, acrylonitrile and acrolein) were obtained as described [3].

$[PtCl_2(R,R\text{-diam})(\text{methylacrylate})]$ was prepared by dissolving $[PtCl_2(R,R\text{-diam})(\text{ethylene})]$ in the minimum amount of benzene and adding an excess of methylacrylate. After 24 h standing at room temperature, the solution was concentrated *in vacuo* and the solid residue was recrystallized from methylene chloride/n-heptane. The title complex was obtained as yellow microcrystals in 80% yield.

^1H NMR spectrum (δ): 7.3 (m, two C_6H_5); 5.10 and 4.89 (two q, two $C\mathit{H}CH_3$); 4.95 (m, =CH–); 4.07 and 3.67 (two d, $=CH_2$); 3.76 (s, OCH_3); 3.05 and 1.85 (two m, $N{-}CH_2{-}CH_2{-}N$); 2.66 and 2.65 (two s, two NCH_3); 2.04 and 1.96 (two d, two $CHC\mathit{H}_3$).

X-ray Data Collection and Structure Determination

Crystal data and other experimental details are summarized in Table III. The diffraction experiment was carried out on an Enraf-Nonius CAD-4 diffractometer at room temperature using Mo Kα radiation (λ = 0.71073 Å). The calculations were performed on a PDP11/34 computer using an SDP-plus Structure Determination Package [9]. The diffracted intensities were corrected for Lorentz, polarization and absorption (empirical correction [10]). Anomalous dispersion corrections for atomic scattering factors of Pt, Cl, C and N atoms were taken from ref. 11. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares, minimizing the function $\Sigma w(F_o - k|F_c|)^2$. Weights assigned to individual observations were: $w = 1/[\sigma(F_o)]^2$ where $\sigma(F_o) = [\sigma^2(I) + (0.04\,I)^2]^{1/2}/2F_o\mathrm{Lp}$. Anisotropic thermal factors were refined for all the non-hydrogen atoms with the exception of the phenyl ring [C(111)–C(116)]. All the hydrogen atoms were introduced in the model as seen in a difference Fourier map but they were not refined. The determination of the absolute configuration was performed directly by independent refinement of the two structure models, related by inversion. It yielded significantly different results in full agreement with the known absolute configuration of the chelating ligand (*R,R*-diam). The rejected enantiomer gave the following agreement indices: $R = 0.025$, $R_w = 0.036$. The final difference Fourier showed a residual peak close to the platinum atom of 0.9 e/Å^3, all the other being less than 0.3 e/Å^3. The atomic coordinates of the refined model are listed in Table IV.

TABLE III. Crystal Data and Intensity Collection Parameters

Formula	$C_{24}H_{28}Cl_2N_4Pt \cdot C_6H_6$
Molecular mass	716.63
Crystal system	monoclinic
Space group	*C*2
a (Å)	17.842(2)
b (Å)	8.466(1)
c (Å)	10.464(1)
β (°)	109.34(1)
V (Å^3)	1491(6)
Z	2
D_{calc} (g cm^{-3})	1.596
μ(Mo Kα)	49.57
Min. transmission factor	0.51
Scan mode	$\omega/2\theta$
ω scan width (°)	$0.80 + 0.35 \tan \theta$
θ range (°)	2.5–28
Octants of reciprocal space explored	$\pm h, +k, +l$
Measured reflections	2032
Unique observed reflections with $I > 3\sigma(I)$	1943
Final *R* and R_w indices[a]	0.020, 0.028
No. variables	148
e.s.d.[b]	1.264

[a] $R = \Sigma(F_o - k|F_c|)/\Sigma F_o$; $R_w = [\Sigma w(F_o - k|F_c|)^2/\Sigma w F_o^2]^{1/2}$. [b] e.s.d. $= [\Sigma w(F_o - k|F_c|)^2/(NO - NV)]^{1/2}$.

TABLE IV. Atomic Coordinates[a]

Atom	*x*	*y*	*z*
Pt	0.000	0.000	0.000
Cl	−0.01699(6)	0.0114(3)	0.2097(1)
N(1)	0.0871(2)	−0.2052(5)	0.0739(4)
N(4)	0.1510(3)	0.3292(8)	−0.0496(7)
C(1)M	0.1361(3)	−0.2324(9)	−0.0157(6)
C(1)	0.0350(3)	−0.3419(6)	0.0670(6)
C(2)	0.0423(3)	0.2287(6)	0.0429(6)
C(2)M	0.1952(4)	−0.0425(8)	0.2369(9)
C(3)	0.1026(3)	0.2808(7)	−0.0129(6)
C(11)	0.1427(3)	−0.1875(7)	0.2215(6)
C(111)	0.1867(3)	−0.3380(8)	0.2758(6)
C(112)	0.2613(4)	−0.377(1)	0.2575(7)
C(113)	0.3026(4)	−0.513(1)	0.3171(7)
C(114)	0.2655(4)	−0.625(1)	0.3745(8)
C(115)	0.1955(4)	−0.588(1)	0.3939(7)
C(116)	0.1571(3)	−0.4436(8)	0.3455(6)

[a] e.s.d.s given in parentheses.

Supplementary Material

Listing of anisotropic thermal parameters, as well as the observed and calculated structure factors, may be obtained from the authors.

Acknowledgements

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