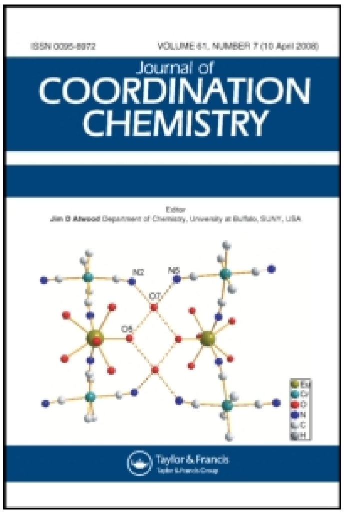

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and crystal structure of *trans*-dichloro(1,3-propylenediamine-*n,n'*-diacetato)platinum(IV) monohydrate

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To cite this Article Đinović, Vesna M. , Bogdanović, Goran A. , Novaković, Slađana and Sabo, Tibor J.(2004) 'Synthesis and crystal structure of *trans*-dichloro(1,3-propylenediamine-*n,n'*-diacetato)platinum(IV) monohydrate', Journal of Coordination Chemistry, 57: 7, 535 — 541

To link to this Article: DOI: 10.1080/00958970410001671110

URL: http://dx.doi.org/10.1080/00958970410001671110

J. Coord. Chem., Vol. 57, No. 7, 10 May 2004, pp. 535–541

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SYNTHESIS AND CRYSTAL STRUCTURE OF *trans*-DICHLORO(1,3-PROPYLENEDIAMINE-*N*,*N*′-DIACETATO)PLATINUM(IV) MONOHYDRATE

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(Received 3 December 2003)

The *trans*-geometrical isomer of the first Pt(IV) complex with the tetradentate ligand 1,3-propylenediamine-*N*,*N*′-diacetate ion (pdda) was prepared by a direct synthesis from potassium hexachloroplatinate(IV) and pdda in the presence of lithium hydroxide. The crystal structure of *trans*-$[Pt(pdda)Cl_2] \cdot H_2O$ complex has been determined. The Pt(IV) ion has a distorted octahedral coordination due to intramolecular N–H···Cl interactions.

Keywords: Platinum(IV) complex; Crystal structure; Edda ligands

1. INTRODUCTION

Geometrical isomerism in metal complexes of linear flexible tetradentate ligands of the donor atom array ONNO such as edda (ethylenediamine-*N*,*N*′-diacetate ion), eddp (ethylenediamine-*N*,*N*′-di-3-propionate ion) or pdda (1,3-propylenediamine-*N*,*N*′-diacetate ion) has been studied by a number of authors [1–14]. Such ligands can occupy four of the octahedral sites around a central ion and the other two sites may be occupied by other ligands, in which three geometrical isomers are possible, as shown in Fig. 1.

The chelating ability of ethylenediamine-*N*,*N*′-diacetic acid was first investigated by Chaberek and Martell [15]. In most synthetic routes [1–14] edda takes a symmetric coordination position (*s-cis*) rather than an unsymmetric one (*uns-cis*) [3]. It has been suggested that the observed chelate strain of carboxylate rings in *uns-cis*-edda

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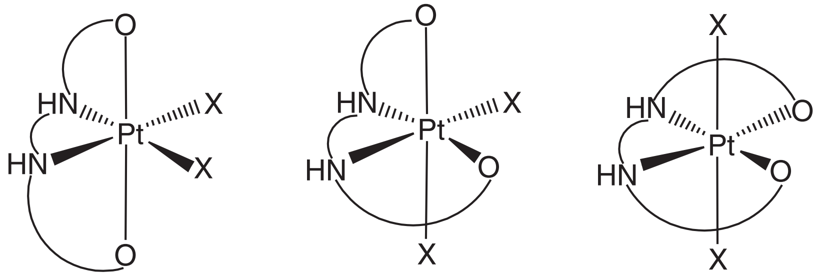
ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970410001671110



I
s-cis

II
uns-cis

III
trans

FIGURE 1 Possible geometrical isomers of [Pt(pdda)X_2] complexes.

complexes may be a contributing factor in determining the configuration of the edda ligand [6]. However, the pdda ligand, with a longer diamine moiety than edda, prefers unsymmetric coordination [16,17], suggesting that the size of the edda chelate ring has a profound effect on the distribution of the geometrical isomers. Investigations by Liu [18] indicate that in the case of platinum(IV) complexes with edda, the *cis*-dichloro isomer is more abundant. He found that oxidation of the edda–platinum(II) complex can also give a *cis*-dichloro isomer. However, the first synthesized platinum(IV) complex with eddp contained the *trans*-geometric isomer [13].

The discovery of the tumour-inhibiting properties of cisplatin by Rosenberg and coworkers over 30 years ago was a major catalyst for the study of metal complexes as antitumor drugs. [19,20] and this has prompted us to reinvestigate some of these complexes. In this article, the preparation of *trans*-dichloro(1,3-propylenediamine-*N*,*N*′-diacetato)platinum(IV), using the same method as Liu, is reported. The geometric configuration of the isolated complex is assigned on the basis of its electronic absorption, infrared spectra and an X-ray structural study.

2. EXPERIMENTAL

Reagents were obtained commercially and used without further purification.

2.1. *trans*-Dichloro(propylenediamine-*N*,*N*′-diacetato)platinum(IV)monohydrate, *trans*-[Pt(pdda)Cl_2]·H_2O

Some 0.200 g of potassium hexachloroplatinate(IV) (0.41 mmol) and 0.093 g of pdda · 2HCl (0.41 mmol) were dissolved in 25 cm^3 of water. The reaction mixture was heated on a steam bath for 12 h during which period 15.68 cm^3 of aqueous 0.105 mol dm^{-3} LiOH (1.65 mmol) were added in small portions. The solution was then filtered and evaporated on a steam bath until crystallization commenced. After cooling, the crystals were filtered off, washed thoroughly with water and air dried. Yield: 0.140 g (72.3%). *Anal*. Calcd. for *trans*-[Pt(pdda)Cl_2] · H_2O (%): C, 17.67; H, 3.40; N, 5.83. Found: C, 17.80; H, 3.00; N, 5.93.

TABLE I Crystal data, data collection and structural refinement details for *trans*-[Pt(pdda)Cl_2]$\cdot H_2O$

Formula	$C_7H_{14}Cl_2N_2O_5Pt$	V (Å^3)	12 141.5(6)
M	472.19	Z	4
Colour; habit	Yellow; prismatic	Dc (Mg/m^3)	2.526
Crystal size (mm)	$0.56 \times 0.50 \times 0.20$	μ(Mo Kα) (mm^{-1})	11.743
T (K)	293(2)	F(000)	888
λ (Å)	0.71073	θ range (°)	2.20–25.97
Space group	$P2_1/n$	Index ranges	$0 \leq h \leq 8$, $-4 \leq k \leq 15$, $-15 \leq l \leq 15$
a (Å)	7.226(3)	Reflections collected	3504
b (Å)	13.643(2)	Independent reflections for $I > 2\sigma(I)$	2410(2180)
c (Å)	12.604(2)	Data/restraints/parameters	2410/0/154
		Goodness-of-fit on F^2	1.101
β (°)	92.38(2)	Final R indices for $I > 2\sigma(I)$	$R1 = 0.0525$, $wR2 = 0.1375$
		R indices (all data)	$R1 = 0.0599$, $wR2 = 0.1431$

2.2. Spectroscopic Measurements

Infrared spectra were recorded on a Perkin-Elmer FTIR 31725-X spectrophotometer using the KBr pellet technique. Electronic absorption spectra were recorded on a Varian GBC 911A spectrophotometer. For this measurement a 5×10^{-5} mol dm^{-3} aqueous solution of the complex was used.

2.3. X-ray Crystallography

Data were collected on an Enraf-Nonius CAD-4 diffractometer [22] using Mo Kα radiation ($\lambda = 0.71069$ Å) and $\omega/2\theta$ scans in 2.20–25.97° θ range. Cell constants and an orientation matrix for data collection, obtained from 23 centred reflections in the range 14.66–19.88°, corresponded to a monoclinic cell whose dimensions are given in Table I. The data were corrected for Lorentz and polarization effects [21]. A Gaussian-type absorption correction [23,24] based on the crystal morphology was applied ($T_{\min} = 0.0211$, $T_{\max} = 0.1252$).

The structure was solved by heavy-atom [25] and difference Fourier methods and refined on F^2 by full-matrix least-square methods [26]. Final atomic coordinates and equivalent isotropic displacement parameters for *trans*-[Pt(pdda)Cl_2]$\cdot H_2O$ are given in Table II. All H atoms in the complex were placed at calculated positions and were refined with isotropic displacement parameters set to 1.2 times the equivalent isotropic U value of the parent atom. Water H-atom positions were determined by the HYDROGEN program [27] and were refined using a riding model with a fixed O–H bond length of 0.85 Å; isotropic displacement parameters were set equal to 1.5 times the equivalent isotropic displacement parameter of the parent atoms. Software used to prepare material for publication included PARST [28], WinGX [29] and ORTEPIII [30].

3. RESULTS AND DISCUSSION

Three geometrical isomers of pdda–Pt(IV) complexes with two identical monodentate ligand are theoretically possible, *s-cis*, *uns-cis* and *trans* (Fig. 1). Reaction of $K_2[PtCl_6]$ and pdda produced only one isomer. This isomer, *trans*-[Pt(pdda)Cl_2], was

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters of non-H atoms ($\text{Å}^2 \times 10^3$) for *trans*-$[Pt(pdda)Cl_2] \cdot H_2O$. *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

	x/*a*	*y*/*b*	*z*/*c*	*U*(*eq*)
Pt	1896(1)	3125(1)	8231(1)	21(1)
Cl1	878(5)	1958(2)	7022(2)	36(1)
Cl2	2880(3)	4299(2)	9453(2)	34(1)
O1	3643(10)	3689(6)	7159(6)	32(2)
O2	3987(11)	4947(6)	6119(6)	42(2)
O3	3751(11)	2176(6)	8892(6)	34(2)
O4	4313(12)	1270(6)	10 310(6)	42(2)
C1	3110(14)	4505(8)	6755(7)	31(3)
C2	1245(15)	4873(8)	7081(8)	33(2)
C3	−1407(15)	4439(9)	8169(9)	37(2)
C4	−2378(15)	3624(9)	8728(9)	36(3)
C5	−1310(16)	3173(9)	9650(10)	37(3)
C6	1447(16)	2112(9)	10 187(9)	36(3)
C7	3272(17)	1816(7)	9801(8)	28(2)
N1	123(12)	4095(6)	7517(6)	28(2)
N2	215(12)	2537(6)	9304(6)	26(2)
O5	−2360(12)	975(7)	8998(8)	51(2)

synthesized in high yield. The fact that during this synthesis the *s-cis* and *uns-cis* were not detected can be explained as being due to non-bonding interactions between hydrogens bonded to nitrogen atoms and chloro ligands.

3.1. Electronic Spectra

The two spin-allowed transitions in a low-spin d^6 system in an octahedral crystal field are ${}^1A_{1g} \to {}^1T_{1g}$ and ${}^1A_{1g} \to {}^1T_{2g}$ in order of increasing energy. In a tetragonal field, the degeneracies of the excited states are removed, i.e., ${}^1T_{1g} = {}^1A_{2g} + {}^1E_g^a$ and ${}^1T_{2g} = {}^1B_{2g} + {}^1E_g^b$. With further decrease of molecular symmetry further splitting is expected. As has been shown, small differences between states do not cause splitting of absorption bands, especially of complexes with edta-type ligands and derivatives with lower symmetry than D_{4h} [6]. The electronic absorption spectrum of *trans*-$[Pt(pdda)Cl_2]$ complex shows two bands at 250 and 343 nm.

3.2. Infrared Spectra

The asymmetric stretching frequencies of the carboxylate moieties were established as criteria for distinguishing between protonated carboxylate groups (1700–1750 cm^{-1}) and coordinated carboxylate groups (1600–1700 cm^{-1}) [31]. The complex showed a doublet at 1696 and 1660 cm^{-1} in the asymmetric CO stretching region. Lack of absorption between 1700–1800 cm^{-1} indicates that the carboxyl groups are coordinated to the central platinum(IV) ion. The asymmetric stretching bands of the carboxylate groups of the five-membered chelate rings lie at higher energy than the corresponding bands of six-membered chelate rings [32–36]. Symmetric stretching bands of the coordinated carboxylate groups are found in the expected region (about 1400 cm^{-1}). Amino stretches are observed at 3435 cm^{-1}.

3.3. Description of the Structure

Coordination around platinum(IV) is deformed for the same reasons found for the *trans*-[Pt(eddp)Cl_2] complex [13]. Important bond lengths and angles for *trans*-[Pt(pdda)Cl_2]$\cdot H_2O$ are given in Table III. The structure of the complex is shown in Fig. 2. Although the chlorine atoms are coordinated in *trans* positions they do not occupy the same position in relation to equatorial plane of ONNO ligand. Cl1 is closer to the N1 and N2 atoms than is the case with Cl2. Thus the angles N2–Pt–Cl1 [89.1(2)°] and N1–Pt–Cl1 [88.8(3)°] are smaller than N2–Pt–Cl2 [90.3(2)°] and N1–Pt–Cl2 [90.8(2)°]. This comes as somewhat of a surprise because H atoms

TABLE III Selected geometrical parameters (Å, °) for the complex

Bond distances (Å)		*Bond angles* (°)	
Pt–O3	2.019(7)	O3–Pt–O1	95.6(3)
Pt–O1	2.037(7)	O3–Pt–N2	82.9(3)
Pt–N2	2.021(8)	O1–Pt–N	178.4(3)
Pt–N1	2.026(8)	O3–Pt–N1	177.3(3)
Pt–Cl1	2.303(3)	O1–Pt–N1	81.8(3)
Pt–Cl2	2.313(3)	N2–Pt–N1	99.8(3)
O1–C1	1.276(13)	O3–Pt–Cl1	91.0(3)
O2–C1	1.206(12)	O1–Pt–Cl1	90.7(2)
O3–C7	1.307(14)	N2–Pt–Cl1	89.1(2)
O4–C7	1.222(13)	N1–Pt–Cl1	88.8(3)
C1–C2	1.511(14)	O3–Pt–Cl2	89.3(3)
C2–N1	1.457(14)	O1–Pt–Cl2	89.9(2)
C3–N1	1.480(13)	N2–Pt–Cl2	90.3(2)
C3–C4	1.506(17)	N1–Pt–Cl2	90.8(2)
C4–C5	1.500(17)	Cl1–Pt–Cl2	179.26(10)
C5–N2	1.482(13)		
C6–N2	1.512(13)		
C6–C7	1.480(17)		

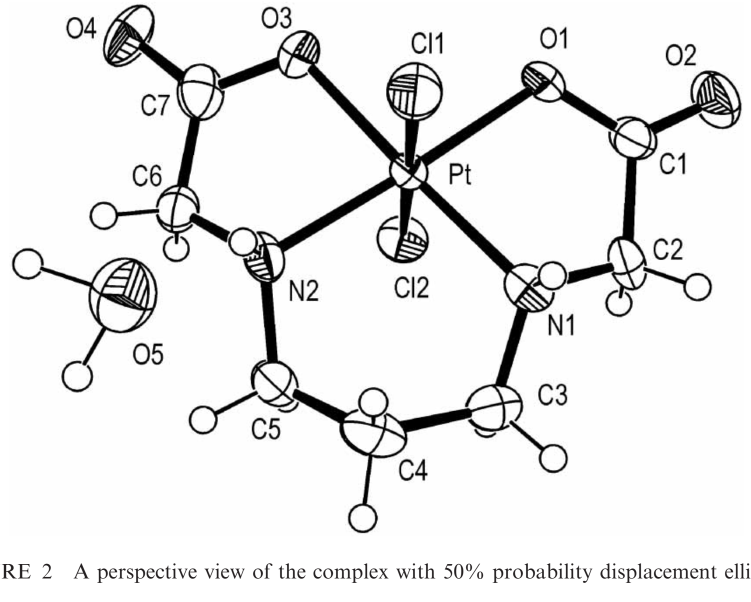


FIGURE 2 A perspective view of the complex with 50% probability displacement ellipsoids.

TABLE IV Hydrogen-bonding geometry (Å, °) for the complex

	D–H	*D···A*	*H···A*	*D–H···A*
N1–H···Cl1^{i}	0.91(1)	3.04(1)	2.65(1)	106.3(5)
N2–H···Cl1^{i}	0.91(1)	3.04(1)	2.65(1)	106.8(5)
C4–H···Cl2^{iii}	0.97(1)	3.70(1)	2.74(1)	168.7(6)
N2–H···O5^{i}	0.91(1)	2.84(1)	2.04(1)	147.4(6)
O5–H1···O2^{ii}	0.85(1)	3.08(1)	2.92(1)	92.3(7)
O5–H2···O4^{iii}	0.85(1)	3.00(1)	2.68(1)	104.2(6)
N1–H···O4^{iv}	0.91(1)	2.86(1)	2.07(1)	144.9(5)
C6–H···O2^{ii}	0.97(1)	3.55(2)	2.58(1)	174.1(8)

Symmetry codes: $^{i}x, y, z$; $^{ii}x-1/2, -y+1/2, z+1/2$; $^{iii}x-1, y, z$; $^{iv}x-1/2, -y+1/2, z-1/2$.

connected to N1 and N2 are turned towards Cl1 (which may represent steric strain, in the absence of any stabilizing interaction). An explanation lies in intramolecular interaction of the N–H···Cl type (Table IV) which stabilizes the structure coordination and which has been noted in the case of *trans*-[Pt(eddp)Cl_2] [13].

The Pt–O1–C1–C2–N1 chelate ring shows a twisted conformation (around the Pt–N1 bond) while another five-membered ring displays an N2-envelope conformation. Puckering parameters [37] of five-membered chelate rings are $Q = 0.338(8)$ Å, $\phi = 333.0(17)°$ for Pt–O1–C1–C2–N1; and $Q = 0.305(9)$ Å, $\phi = 152.0(2)°$ for Pt–O3–C7–C6–N2. This is an interesting result, bearing in mind that both five-membered rings have the same composition and position with respect to the central six-membered chelate ring. The reason for this cannot be due to the conformation of the six-membered ring because it assumes the chair conformation with a pseudo plane of symmetry that bisects the ring through the Pt···C4 line. However, the dissimilarity in the conformation of the five-membered chelate rings can be explained by different intra- and intermolecular interactions of corresponding atoms from both rings. O2 forms only one hydrogen bond while its equivalent from the other ring, O4, forms two strong intermolecular hydrogen bonds (Table IV). The N1–H group forms a hydrogen bond to a carboxyl group from a neighbouring molecule while N2–H is hydrogen-bonded to the water molecule. Relevant weak C–H···O interaction exists only for the Pt–O3–C7–C6–N2 chelate ring (Table IV). The N–H groups for both of chelate rings form intramolecular N–H···Cl interaction type previously observed for *trans*-[Pt(eddp)Cl_2] [13]. Observed differences in conformation of the five-membered chelate rings indicate that intermolecular interactions can have significant influences on coordination and molecular geometry.

Acknowledgments

The authors are grateful to the Ministry of Science and Technology of the Republic of Serbia for financial support (Projects 1253 and 1318).

Supplementary Material

Atomic coordinates, anisotropic thermal parameters and a complete list of the bond distances and angles have been deposited with the Cambridge Crystallographic Data Centre, number 224693.

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