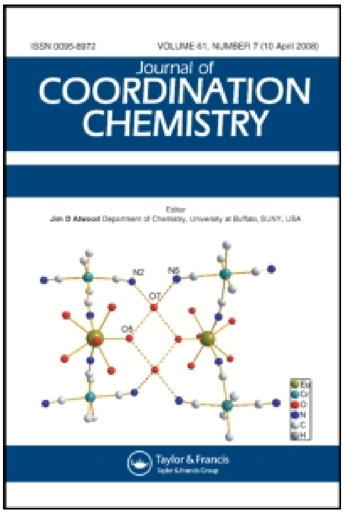

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SYNTHESIS AND CRYSTAL STRUCTURE OF *TRANS*-DICHLORO(ETHYLENEDIAMINE--*N*,*N*′-DI-3-PROPIONATO)PLATINUM(IV) MONOHYDRATE

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This paper reports the first synthesized Pt(IV) complex with ethylenediamine-*N*,*N*′-di-3-propionato ligand (eddp). The crystal structure of *trans*-$[Pt(eddp)Cl_2] \cdot H_2O$ complex has been determined. Pt(IV) has a distorted octahedral coordination due to an intramolecular N–H$\cdots$Cl interaction.

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

INTRODUCTION

Ethylenediamine-*N*,*N*′-di-3-propionate is a tetradentate ligand similar to ethylenediamine-*N*,*N*′-diacetate. A series of complex compounds of cobalt(III) involving these ligands has been widely investigated [1–9]. Geometrical isomerism in metal complexes of linear tetradentate ligands having the donor atom array ONNO such as in edda or eddp has been an interesting field studied by a number of workers [1–11]. Such ligands can occupy four of the octahedral sites around a metal ion and the other two sites may be occupied by other ligands, to form three geometrical isomers, as shown in Fig. 1.

The chelating ability of ethylenediamine-*N*,*N*′-diacetic acid was first investigated by Chaberek and Martell [10]. A study by Liu [11], concerned complexes of ethylenediamine-*N*,*N*′-diacetic acid and platinum(II) and platinum(IV). Edda complexes have been isolated in three geometries [11], (*trans*, *s*-*cis* and *uns*-*cis*). It was noted that complexes containing eddp prefer the *uns*-*cis* configuration, suggesting that the size of the chelate ring has a profound effect on the distribution of geometric isomers [1–9].

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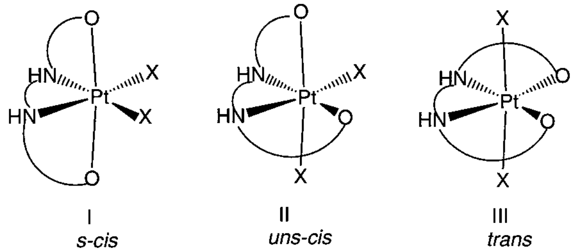

FIGURE 1 Possible geometrical isomers of [Pt(eddp)X_2] complexes.

It has been known since the early studies of Rosenberg and his colleagues that platinum(IV) complexes exhibit substantial anticancer activity [12,13]. Although platinum(II) anticancer drugs are more widely studied [14,15] and used clinically, it has been known since the original discovery that platinum(IV) compounds are also antitumor active. The newest platinum(IV) compounds being tested are the so-called ammine/amine platinum(IV) dicarboxylates [16,18]. Since the discovery that several *trans*-platinum complexes, including JM315 [19], exhibit non-cross-resistance to cisplatin, such complexes have attracted considerable interest in terms of synthesis and biological testing.

Investigations by Liu indicate that in the case of platinum(IV) complexes with edda, the *cis*-dichloro isomer [11] is more abundant. He found that oxidation of edda-platinum(II) can also give a *cis*-dichloro isomer. In this paper such an unexpected synthesis occurred in that, using the same method of Liu with dichloro(ethylenediamine-*N*,*N*′-di-3-propionato)platinum(IV), we synthesized a *trans*-dichloro isomer, [Pt(eddp)Cl_2]. The geometric configuration of the isolated complex is assigned on the basis of its electronic absorption and infrared spectra and an X-ray structural study.

EXPERIMENTAL

Materials

Reagents were obtained commercially and used without further purification.

Trans-dichloro(ethylenediamine-N,N′-di-3-propionato)platinum(IV) monohydrate, trans-[Pt(eddp)Cl_2*]·*H_2O Some 0.200 g of potassium hexachloroplatinate(IV) (0.41 mmol) and 0.114 g of ethylenediamine-*N*,*N*′-di-3-propionic acid dihydrochloride (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 15.68 cm^3 of 0.105 mol dm^{-3} LiOH (1.65 mmol) solution was added in small portions. The solution was then filtered and evaporated on a steam bath until crystallization started. After cooling, the crystals were filtered off, washed thoroughly with water, and air dried. Yield: 0.188 g (97.92%). *Anal.* Calc. for *trans*-[Pt(eddp)Cl_2] (%): C, 20.52; H, 3.01; N, 5.98. Found: C, 20.99; H, 3.51; N, 5.88.

Spectroscopic Measurements

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

X-ray Crystallography

Intensities were measured on a yellow, single crystal with an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator [$\lambda(\mathrm{MoK}\alpha) = 0.71073$ Å]. A summary of crystal data and experimental details is listed in Table I. Intensities of 3227 unique reflections were collected in the range $0 < \theta < 28°$ [21,22]. A gaussian absorption correction [23,24] based on the crystal morphology was applied. The structure was solved by the heavy-atom method using SHELXS86 [25], and refined by SHELXL97 [26,27] to a final $R1 = 0.034$ for 2414 ($I > 2\sigma(I)$) independent reflections and 171 parameters. All significant residual peaks (higher than 0.66 e/Å^3) in the final difference Fourier map were located near the Pt atom. Final atomic coordinates and equivalent isotropic displacement parameters (Å^2) for *trans*-[Pt(eddp)Cl$_2$] · H$_2$O are given in Table II.

RESULTS AND DISCUSSION

Three geometrical isomers of eddp-Pt(IV) complexes with two identical monodentate ligands are theoretically possible, *s-cis*, *uns-cis* and *trans* (Fig. 1). Reaction of K$_2$[PtCl$_6$] and eddp produced only one isomer. This isomer, *trans*-[Pt(eddp)Cl$_2$], was synthesized in high yield. The fact that during this synthesis the *s-cis* and *uns-cis* species were not detected can be explained as being due to non-bonding interactions between hydrogens bonded to nitrogen atoms and chloro ligands.

Electronic Spectra

The two spin-allowed transitions in a low-spin d^6 system in an octahedral crystal field are ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ 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 decreasing molecular symmetry further splitting is

TABLE I Crystal data and data collection details for *trans*-[Pt(eddp)Cl$_2$] · H$_2$O

Formula	$C_8H_{16}N_2O_5Cl_2Pt$	Z	4
M	486.22	D_c (Mg m^{-3})	2.398
Crystal system	monoclinic	λ (Å)	0.71073
Space group	$P2_1/n$	$\mu(\mathrm{MoK}_\alpha)$ (mm^{-1})	10.827
a (Å)	7.1104(12)	Scan mode	$\omega/2\theta$
b (Å)	11.608(2)	θ range (°)	2.15–27.98
c (Å)	16.334(4)	Data collcd.	6501
α (°)	90	independent reflextions	3227
β (°)	92.28(1)	having $I > 2\sigma(I)$	2414
γ (°)	90	S[a]	1.002
V (Å^3)	1347.0(4)	R[b]	0.0343
F(000)	920	R_w[c]	0.0709

[a] $S = GooF = \{[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$;
[b] $R = \sum \|F_o\| - \|F_c\| / \sum |F_o|$;
[c] $R_w = \{[\sum w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{0.5}$; $w = 1/[\sigma^2(F_o^2) + (0.0349P)^2]$, where $P = (F_o^2 - 2F_c^2)/3$.

TABLE II Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for *trans*-[Pt(eddp)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)*
Pt1	0.0600(1)	0.0991(1)	0.2268(1)	0.021(1)
Cl1	0.3382(3)	0.1250(1)	0.3008(1)	0.035(1)
Cl2	−0.2194(3)	0.0700(1)	0.1531(1)	0.037(1)
O1	0.1727(8)	−0.0381(3)	0.1704(3)	0.031(1)
O3	−0.0193(7)	−0.0170(4)	0.3110(3)	0.033(1)
N1	0.1277(8)	0.2138(4)	0.1395(3)	0.026(1)
N2	−0.0344(8)	0.2396(4)	0.2866(3)	0.027(1)
O2	0.3569(8)	−0.1225(4)	0.0855(3)	0.039(1)
O4	−0.1466(10)	−0.0728(5)	0.4226(4)	0.057(2)
C1	0.2768(11)	−0.0348(5)	0.1072(4)	0.029(2)
C2	0.2915(14)	0.0748(5)	0.0551(5)	0.039(2)
C3	0.3058(11)	0.1883(5)	0.0998(5)	0.031(2)
C4	0.1144(11)	0.3325(5)	0.1754(5)	0.030(2)
C5	−0.0568(11)	0.3342(5)	0.2259(5)	0.034(2)
C6	−0.1999(11)	0.2167(6)	0.3353(5)	0.041(2)
C7	−0.1553(14)	0.1284(6)	0.4007(5)	0.047(2)
C8	−0.1053(12)	0.0039(6)	0.3762(5)	0.036(2)
O5	0.0932(11)	−0.2839(6)	−0.0018(4)	0.059(2)

expected. As has been shown, small differences between states do not cause significant splitting of the absorption bands, especially of complexes with edta-type ligands and derivatives with lower symmetry than D_{4h} [5]. The electronic absorption spectrum of *trans*-[Pt(eddp)Cl_2] complex shows two bands at 250 and 350 nm.

Infrared Spectra

A doublet of strong absorptions at 1637 cm^{-1} and 1630 cm^{-1} was observed in CO stretching region. The lack of absorption between 1700–1800 cm^{-1} indicates that the carboxyl groups of eddp are definitely coordinated to the central platinum(IV) ion [20]. The symmetric stretching bands of the coordinated carboxylate groups lie in the expected region (about 1400 cm^{-1}). Amino stretches are observed at 3446 cm^{-1}.

Description of the Structure

The N1, N2, O1, O3 atoms of the eddp ligand are not more than 0.06 Å from the least-squares plane they define. However, it is interesting that the Pt–Cl bonds, expected to form angles near 90° with respect to the coordinated atoms of the eddp ligand show significant deviations, and N1–Pt–Cl1 (93.5°) and N2–Pt–Cl1 (86.3°) angles deviate by some way (Table III). This can be explained by intramolecular interaction between N2–H$\cdots$Cl1 (H$\cdots$Cl1 = 2.569(1) Å, N2–H$\cdots$Cl1 = 106.9(2)°) and N1–H$\cdots$Cl2 (H$\cdots$Cl2 = 2.603(1) Å, N1–H$\cdots$Cl2 = 106.8(2)°). The difference in angles is the more unusual because the N1 and N2 atoms are chemically and structurally identical. These interactions, most probably, stabilize the obtained isomer and conformation of the chelating ligand. Conformation of the eddp ligand constrains hydrogen atoms bonded to N1 and N2 to axial orientations.

The oxygen atom of the water of crystallization makes three hydrogen bonds. In one, it participates as a donor (O5$^{i}\cdots$O2^{i} = 2.98 Å, O5$^{i}\cdots$O4^{ii} = 2.81 Å, O2$\cdots$O5$\cdots$O4 = 99.8°). In another, it is a H bond acceptor (N1$^{i}\cdots$O5^{iii} = 2.81 Å, H$^{i}\cdots$O5^{iii} = 2.00 Å,

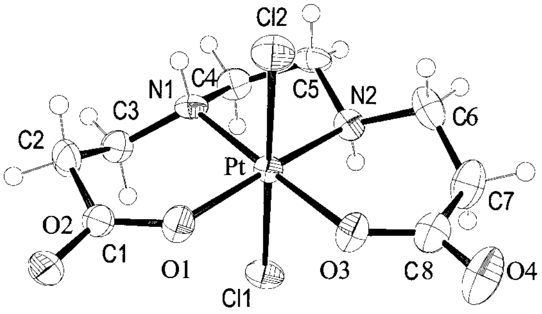

FIGURE 2 A perspective view of the complex with 50% probability displacement ellipsoids.

TABLE III Selected bond parameters for the complex

Bond Distances(Å)		*Bond Angles(°)*	
Pt–O1	2.022(4)	N1–Pt–Cl1	93.5(2)
Pt–O3	2.021(4)	N1–Pt–Cl2	87.3(2)
Pt–N1	2.023(5)	N1–Pt–N2	84.4(2)
Pt–N2	2.029(5)	N1–Pt–O1	95.0(2)
Pt–Cl1	2.296(2)	N2–Pt–Cl1	86.3(2)
Pt–Cl2	2.307(2)	N2–Pt–Cl2	94.3(2)
O1–C1	1.295(8)	N2–Pt–O3	95.9(2)
O3–C8	1.273(8)	O1–Pt–O3	84.9(2)
O2–C1	1.226(7)	Cl1–Pt–Cl2	179.09(6)
O4–C8	1.212(9)	N1–Pt–O3	177.3(2)
(N2)H···Cl1	2.569(1)	N2–Pt–O1	175.9(2)
(N1)H···Cl2	2.603(1)	N2–H···Cl1	106.9(2)
		N1–H···Cl2	106.8(2)

N1–H···O5 = 147.0°). The O2 atom make one more significant intermolecular H bond: N2^{i}···O2^{iv} = 2.88 Å, H2^{i}···O2^{iv} = 2.09 Å, N2–H···O2 = 145.6° (Fig. 2).

Supplementary Material

Atomic coordinates, anisotropic thermal parameters, structure factors and a complete list of the bond distances and angles have been deposited with the Cambridge Crystallographic Data Centre number 154044.

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