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The Crystal and Molecular Structures of Dichloro[*N*,*O*-(D,L)-diaminopropionic acid]platinum(II) and Dichloro[*N*,*O*-(L)-lysine]platinum(II) Monohydrate

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Abstract

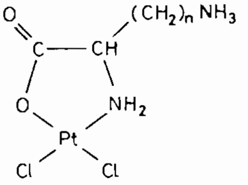
K_2PtCl_4 reacts with L-lysine and with D,L-diaminiopropionic acid (Dap) forming the neutral complexes $[PtCl_2(N,O\text{-Lys})]\cdot H_2O$ (**1**) and $[PtCl_2(N,O\text{-Dap})]$, (**2**) respectively.

Compound **1** is monoclinic, space group $P2_1$ with $a = 11.262(3)$, $b = 11.041(2)$, $c = 9.690(2)$ Å, $\beta = 102.07(5)°$, $V = 1178(1)$ Å^3 and $Z = 4$. Compound **2** is monoclinic, space group $P2_1/n$ with $a = 8.777(1)$, $b = 10.615(2)$, $c = 7.947(1)$ Å, $\beta = 94.98(3)°$, $V = 738(1)$ Å^3 and $Z = 4$. In both compounds, the zwitterionic ligands form an N,O-five membered chelate with the platinum atom. Structures **1** and **2** were refined to R values of 3.3% and 6.3% respectively.

Introduction

All basic α-amino acids react with K_2PtCl_4 in a 1:1 molar ratio forming crystalline, inert chelates in which the amino acid is bound to platinum(II) through α-amine and carboxyl oxygen with the terminal positively charged amine unbound [1, 2] (Scheme 1).

The distance of the terminal amine group from the metal center is crucial for the stability of the complex. In the case of diaminopropionic acid (Dap) ($n = 1$) and diaminobutyric acid (Dab) ($n = 2$) rearrangement to N,N-five and N,N-six membered rings respectively occurs easily upon heating in aqueous solution [2]. On the other hand, the ornithine complex ($n = 3$) has no tendency to form N,N-seven-membered ring under the above conditions whereas the lysine complex ($n = 4$) decomposes in hot water [2]. It was therefore interesting to have more structural details for the two extreme cases in which $n = 1$ and $n = 4$. We report here the results of X-ray structural studies of $[PtCl_2(N,O\text{-Lys})]\cdot H_2O$ (**1**) and of $[PtCl_2(N,O\text{-Dap})]$ (**2**).



Scheme 1.

Experimental

$[PtCl_2(N,O\text{-Dap})]$ and $[PtCl_2(N,O\text{-Lys})]$ were prepared according to the published procedures [1, 2] using D,L-diaminopropionic acid monohydrochloride and K_2PtCl_4, purchased from Aldrich, and L-lysine from Ajimoto Co. The crude compounds were ground and recrystallized from hot water (80 °C). Crystals were grown by slow evaporation at room temperature and dried in air until a constant weight was reached. (The hydrated complexes showed a tendency to lose water in high vacuum.) Optical activity of 10 mg/ml sample solutions was measured on a Perkin-Elmer 141 Polarimeter. DL-Dap and $[PtCl_2(N,O\text{-Dap})]$ were inactive, whereas L-lysine monohydrochloride showed optical rotation $[\alpha]_D^{21} + 12.0 \pm 0.5°$, and $[PtCl_2(N,O\text{-Lys})]$ had $[\alpha]_D^{21} - 23.1 \pm 0.5°$.

X-ray Crystallography

Data were measured on a PW1100 Philips four-circle computer-controlled diffractometer. Mo Kα ($\lambda = 0.71069$ Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 20 reflections in the range of $12° \leqslant \theta \leqslant 16°$. Data were measured using the ω–2θ technique.

Intensities were corrected for Lorentz and polarization effects. Absorption correction was applied using the ψ-scan method. The positions of the Pt

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TABLE I. Crystallographic Data

Compound	1	2
Formula	$C_6H_{14}Cl_2N_2O_2Pt \cdot H_2O$	$C_3H_8Cl_2N_2O_2Pt$
Molecular weight	430.20	370.10
Space group	$P2_1$	$P2_1/n$
a (Å)	11.262(3)	8.777(1)
b (Å)	11.041(2)	10.615(2)
c (Å)	9.690(2)	7.947(1)
β (°)	102.07(5)	94.98(3)
V (Å^3)	1178(1)	738(1)
Z	4	4
D_{calc} (g cm^{-3})	2.43	3.33
μ (cm^{-1})	118.60	189.22
Range of 2θ(°)	3–45	3–55
No. of unique data	1631	1679
Data with $F_o^2 > 3\sigma(F_o^2)$	1569	1532
R	0.033	0.063
R_w	0.049	0.087

atoms were obtained from a three-dimensional Patterson function. Refinement* of each structure proceeded to convergence by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where w, F_o and F_c are the weight, the observed and calculated structure factors, respectively. Structure **1** was refined in space group $P2_1$ using anisotropic thermal parameters for all Pt, Cl, O and N atoms and isotropic ones for the carbon atoms. Structure **2** was refined in space group $P2_1/n$ using anisotropic thermal parameters for all non-hydrogen atoms.

The discrepancy indices, $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ are presented with other pertinent crystallographic data in Table I.

Results and Discussion

[PtCl$_2$(L-lysine)]·H$_2$O (1)

With four molecules in the unit cell of space group $P2_1$ there are two independent molecules in the asymmetric unit, and no crystallographic symmetry is imposed upon either one. The atomic positional parameters are listed in Table II and Table III presents the important bond lengths and angles. Figure 1 shows the numbering scheme in molecule 2. The structure and dimensions of the two molecules in the asymmetric unit are similar as can be seen from Table II. In each molecule, the zwitterionic lysine ligand forms an N,O-five membered chelate. The N(amino)–Pt–O(carboxyl) angles in molecules 1 and 2, 84.0(6)° and 82.2(6)° respectively, agree well with the value of 83°, predicted for a mean metal–donor bond distance of 2.0 Å [3]. The Pt and N atoms lie +0.07 and +0.42 Å from the carboxyl plane in molecule 1, and +0.19 and +0.37 Å in molecule 2. The torsion angles about the carboxyl C–C bond in molecules 1 and 2 are 13.9 and 15.6° respectively.

An elaborate network of hydrogen bonds between the terminal NH_3^+ groups, the water molecules of crystallization, the carbonyl oxygen atoms and the chlorine atoms exists in the crystal. The NH_3^+ groups are bonded to C=O groups of neighbouring complexes with N(2)–O(21) and N(21)–O(2) distances of 2.78(1) and 2.79(1) Å respectively.

[PtCl$_2$(Dap)] (2)

The atomic positional parameters are listed in Table IV. Table V presents the bond lengths and angles in the complex. Figure 2 shows the structure and the numbering scheme in the complex. With four molecules in the unit cell of space group $P2_1/n$, there is no crystallographic symmetry imposed upon the complex. The zwitterionic N,O-bonded Dap

TABLE II. Positional Parameters[a] for **1**

Atom	x	y	z	Atom	x	y	z
Pt(1)	0.38274(5)	0.60000	0.06105(5)	Pt(2)	0.10935(5)	0.42991(7)	0.42976(5)
Cl(1)	0.4602(4)	0.7866(5)	0.1425(4)	Cl(11)	0.0500(4)	0.2376(4)	0.3436(4)
Cl(2)	0.3258(5)	0.6675(6)	−0.1656(4)	Cl(21)	0.1663(4)	0.3645(5)	0.6573(4)
O(1)	0.421(1)	0.532(1)	0.258(1)	O(11)	0.071(1)	0.497(1)	0.234(1)
O(2)	0.400(1)	0.374(1)	0.384(1)	O(21)	0.074(1)	0.668(2)	0.112(1)
N(1)	0.324(1)	0.432(2)	0.007(1)	N(11)	0.155(1)	0.608(2)	0.481(1)
N(2)	0.131(1)	−0.141(2)	−0.052(1)	N(21)	0.384(1)	1.176(2)	0.558(1)
C(1)	0.376(1)	0.425(2)	0.270(1)	C(11)	0.083(1)	0.615(2)	0.225(2)
C(2)	0.304(2)	0.364(2)	0.141(2)	C(21)	0.112(1)	0.681(2)	0.358(2)
C(3)	0.332(2)	0.236(2)	0.130(2)	C(31)	0.194(1)	0.796(2)	0.352(2)
C(4)	0.250(2)	0.166(3)	0.008(2)	C(41)	0.215(2)	0.874(2)	0.485(2)
C(5)	0.263(3)	0.028(3)	0.032(3)	C(51)	0.281(2)	0.986(2)	0.454(2)
C(6)	0.209(2)	−0.052(2)	−0.099(2)	C(61)	0.301(1)	1.067(2)	0.586(1)
OW(1)	−0.045(2)	−0.022(2)	0.091(1)	OW(2)	0.571(1)	1.068(2)	0.435(1)

[a] e.s.d.s in the least significant digits are shown in parentheses.

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*All crystallographic computing was done on a CYBER 855 computer at the Hebrew University of Jerusalem, using the SHELX 1977 structure determination package.

TABLE III. Bond Lengths (Å) and Angles (°) for 1

Pt(1)–Cl(1)	2.311(6)	Pt(2)–Cl(11)	2.327(5)
Pt(1)–Cl(2)	2.280(4)	Pt(2)–Cl(21)	2.281(4)
Pt(1)–O(1)	2.01(1)	Pt(2)–O(11)	2.00(1)
Pt(1)–N(1)	2.00(2)	Pt(2)–N(11)	2.07(2)
O(1)–C(1)	1.29(2)	O(11)–C(11)	1.31(2)
O(2)–C(1)	1.22(2)	O(21)–C(11)	1.23(2)
N(1)–C(2)	1.57(2)	N(11)–C(21)	1.43(2)
N(2)–C(6)	1.45(3)	N(21)–C(61)	1.58(3)
C(1)–C(2)	1.50(2)	C(11)–C(21)	1.45(2)
C(2)–C(3)	1.46(3)	C(21)–C(31)	1.57(2)
C(3)–C(4)	1.55(3)	C(31)–C(41)	1.53(2)
C(4)–C(5)	1.55(4)	C(41)–C(51)	1.50(3)
C(5)–C(6)	1.56(3)	C(51)–C(61)	1.54(2)
Cl(1)–Pt(1)–Cl(2)	92.7(2)	Cl(11)–Pt(2)–Cl(21)	93.4(2)
Cl(1)–Pt(1)–O(1)	91.2(4)	Cl(11)–Pt(2)–O(11)	90.6(4)
Cl(1)–Pt(1)–N(1)	175.0(5)	Cl(11)–Pt(2)–N(11)	172.8(4)
Cl(2)–Pt(1)–O(1)	175.3(4)	Cl(21)–Pt(2)–O(11)	175.1(4)
Cl(2)–Pt(1)–N(1)	92.1(5)	Cl(21)–Pt(2)–N(11)	93.7(5)
O(1)–Pt(1)–N(1)	84.0(6)	O(11)–Pt(2)–N(11)	82.2(6)
Pt(1)–O(1)–C(1)	115(1)	Pt(2)–O(11)–C(11)	115(1)
Pt(1)–N(1)–C(2)	109(1)	Pt(2)–N(11)–C(21)	108(1)
O(1)–C(1)–O(2)	119(1)	O(11)–C(11)–O(21)	123(2)
O(1)–C(1)–C(2)	119(1)	O(11)–C(11)–C(21)	117(1)
O(2)–C(1)–C(2)	121(2)	O(21)–C(11)–C(21)	121(2)
N(1)–C(2)–C(1)	109(1)	N(11)–C(21)–C(11)	115(2)
N(1)–C(2)–C(3)	110(1)	N(11)–C(21)–C(31)	113(2)
C(1)–C(2)–C(3)	114(2)	C(11)–C(21)–C(31)	113(1)
C(2)–C(3)–C(4)	116(2)	C(21)–C(31)–C(41)	114(1)
C(3)–C(4)–C(5)	111(2)	C(31)–C(41)–C(51)	107(1)
C(4)–C(5)–C(6)	115(2)	C(41)–C(51)–C(61)	108(1)
N(2)–C(6)–C(5)	107(2)	N(21)–C(61)–C(51)	107(1)

TABLE IV. Positional Parameters[a] for 2

Atom	x	y	z	Atom	x	y	z
Pt	0.41327(4)	0.05465(4)	0.19680(5)	N(1)	0.428(1)	−0.134(1)	0.183(1)
Cl(1)	0.1957(4)	0.0636(3)	0.0176(5)	N(2)	0.536(1)	−0.4057(9)	0.196(1)
Cl(2)	0.4167(3)	0.2712(3)	0.2207(4)	C(1)	0.653(1)	−0.082(1)	0.375(1)
O(1)	0.607(1)	0.0346(9)	0.349(1)	C(2)	0.543(1)	−0.189(1)	0.313(1)
O(2)	0.781(1)	−0.1041(9)	0.445(1)	C(3)	0.633(1)	−0.295(1)	0.247(2)

[a] e.s.d.s in the least significant digits are shown in parentheses.

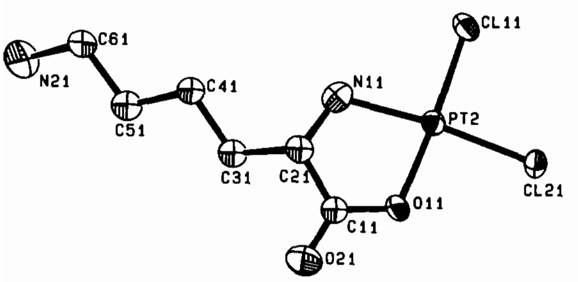

Fig. 1. The structure and the numbering scheme of molecule 2 in [PtCl$_2$(L-Lys)]·H$_2$O.

ligand forms a five membered ring with the platinum atom. The Pt and N atoms lie +0.33 and +0.49 Å from the carboxyl plane respectively and the torsion angle about the carboxyl C–C bond is 19.8°. Hydrogen bonds exist between the terminal NH$_3^+$ group and C=O groups of two neighbouring complexes with N...O distances of 2.93(1) and 2.87(1) Å.

The bond lengths Pt–Cl and Pt–N of compounds 1 and 2 are similar to those found in *cis*-[PtCl$_2$(NH$_3$)$_2$] (Pt–N 2.01(4); Pt–Cl 2.33(1) Å) [4], *cis* [Pt(Cl$_2$(GlyH)$_2$] (Pt–N 2.08(3), Pt–Cl 2.30(1) and 2.27(1) Å) [5], and *cis* [PtCl$_2$(GlyGlyOEt)$_2$]

TABLE V. Bond Lengths (Å) and Angles (°) for **2**

Pt–Cl(1)	2.283(3)	O(2)–C(1)	1.24(1)
Pt–Cl(2)	2.306(3)	N(1)–C(2)	1.50(2)
Pt–O(1)	2.01(1)	N(2)–C(3)	1.49(1)
Pt–N(1)	2.01(2)	C(1)–C(2)	1.54(2)
O(1)–C(1)	1.31(2)	C(2)–C(3)	1.50(2)
Cl(1)–Pt–Cl(2)	90.8(1)	O(1)–C(1)–O(2)	120(1)
Cl(1)–Pt–O(1)	176.0(3)	O(1)–C(1)–C(2)	118(1)
Cl(1)–Pt–N(1)	93.5(3)	O(2)–C(1)–C(2)	122(1)
Cl(2)–Pt–O(1)	93.0(3)	N(1)–C(2)–C(1)	107(1)
Cl(2)–Pt–N(1)	175.4(3)	Ni(1)–C(2)–C(3)	113(1)
O(1)–Pt–N(1)	82.7(4)	C(1)–C(2)–C(3)	109.2(9)
Pt–O(1)–C(1)	115.3(8)	N(2)–C(3)–C(2)	112.4(9)
Pt–N(1)–C(2)	112.9(8)		

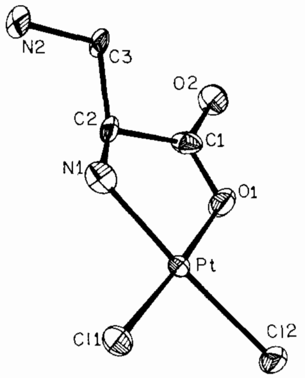

Fig. 2. The structure of [$PtCl_2$(Dap)].

(Pt–N 2.04(1); Pt–Cl 2.296(4) and 2.315(3) Å) [6]. The bond lengths Pt–N and Pt–O are also similar to those found in bicyclic neutral *trans*-[Pt(Gly)$_2$] chelate (Pt–N 2.037(4), Pt–O 2.002(4) Å) [7]. The bond angles N(amino)–Pt–O(carboxyl) in **1** and **2** are similar to those in *trans*-[Pt(Gly)$_2$] (82.5(2)°) [7]. Slight differences are observed in the deviations of the platinum and nitrogen atoms from the carboxyl plane which in *trans*-[Pt(Gly)$_2$] are +0.05 and −0.32 Å respectively. Some deviations also occur in the dimensions of the coordinated lysine in molecule 1 and 2 of [$PtCl_2$(L-Lys)]·H_2O as compared to those of the free ligand in L-Lys·HCl·2H_2O [8], L-lysine–L-aspartate [9] and [Pt-Cl_6]$^{2-}$(lysine 2H)]$^{2+}$ [10]. The bond lengths N(1)–C(2), C(1)–C(2) and C(6)–N(2) in the free L-Lys·HCl·2H_2O are 1.482(4), 1.524(3) and 1.482(4) Å respectively (the N(1)–C(2) and the N(2)–C(6) bonds are equal); in L-lysine–L-aspartate they are 1.515(7), 1.523(9) and 1.512(10) Å (N(1)–C(2) and N(2)–C(6) are also equal); in [$PtCl_6$]$^{2-}$(L-lysine 2H)$^{2+}$ 1.511(4); 1.504(16) and 1.492(17) Å [10]. The corresponding bond lengths for molecule 1 and molecule 2 in **1** are 1.57(2); 1.46(3) 1.45(3) and 1.43(2), 1.57(2) and 1.58(3) Å. Such an alternating pattern of the bond lengths in one unit cell was not observed in [$PtCl_2$(L-Orn)]·2H_2O [11] and in [Cu(L-Orn)$_2$]·H_2O [12]. In [Cu(L-Lys)$_2$]·2H_2O the C–N distances are 1.485(3) and 1.473(3) Å whereas C(sp^3)–C(sp^3) bond lengths range from 1.485(3) to 1.535(3) Å [13].

Supplementary Material

Tables of structure factors and thermal parameters for **1** and **2** (20 pages) are available from the authors on request.

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Note Added in Proof

It has been brought to our attention that crystal structures of (D,L-diaminopropionic acid)$PtCl_2$, (D,L-diaminobutyric acid)$PtCl_2$ and (L-ornithine)$PtCl_2$ were reported by M. Cais, D. Cwikel, I. Agmon and M. Kapon at the 24th ICCC, Athens, 1986, Abstract E3-820.