

Crystal structure of *cis*-dichloro(2,2'-dipyridylamine)-platinum(II)

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Dichloro(2,2'-dipyridylamine)platinum(II) has been prepared and studied by single-crystal X-ray diffraction methods at 293(2) K. The mononuclear complex has a square-planar geometry. The platinum atom is coordinated by two chloride and two nitrogen atom of pyridyl groups in a *cis* fashion. The NH group is not coordinated, but involves in intermolecular hydrogen bonding interaction.

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1 Introduction

A few platinum(II)-2,2'-dipyridylamine complexes are biologically active and potentially antitumor drugs [1, 2]. Their synthesis, spectroscopy, DNA-binding, and cytotoxic properties have been studied. Here we report the crystal structure of dichloro((2,2'-dipyridylamine)platinum(II).

2 Experiment

A mixture of K_2PtCl_4 and 2,2'-dipyridylamine (molar ratio 1:1) in water was heated at 60°C overnight. The resulted yellow solid was collected and washed with water and ethanol, and dried. The crude product was recrystallized from DMF to yield yellow crystals. Yield: 63%. Calc. for $PtCl_2C_{10}H_9N_3$: C, 27.47; H, 2.08; N, 9.61. Found: C, 27.35; H, 2.36; N, 9.31.

Data collection was performed on a Bruker Smart-CCD diffractometer by using monochromatized Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ at room temperature. Data reduction was performed by using the SAINT+ Version 6.02 software [3]. The data were corrected for absorption by using the program SADBAS within the SAINTPLUS package. The structures were solved by the direct method with SHELXS97. This solution yielded platinum atoms. Subsequent Fourier synthesis gave the non-hydrogen atom positions. The hydrogen atoms were geometrically fixed and allowed to ride on their attached atoms, and refined with the XSELL software [4]. The final refinement included anisotropic thermal parameters for all of the non-hydrogen atoms and converged to the $R1$ and $wR2$ values listed in Table 1. The crystal data collection and refinement parameters were summarized in Tables 1. The atomic coordinates are given in Table 2. Selected bond distances and angles are given in Table 3. Thermal parameters of non-hydrogen atoms and hydrogen atom coordinates are listed in Tables 4 and 5, respectively.

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Table 1 Summary of Crystallographic Data.

Empirical formula	C ₁₀ H ₉ Cl ₂ N ₃ Pt
Formula weight	437.19
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2 ₁ /n
Unit cell dimensions	a = 9.978(5) Å α = 90°. b = 10.187(6) Å β = 94.357(8)°. c = 11.807(6) Å γ = 90°.
Volume	1196.7(11) Å ³
Z, Calculated density	4, 2.427 Mg/m ³
Absorption coefficient	12.146 mm ⁻¹
F(000)	808
Crystal size	0.14 x 0.16 x 0.26 mm ³
θ range for data collection	4.76 to 23.89°.
Index ranges	-9 ≤ h ≤ 11, -11 ≤ k ≤ 11, -13 ≤ l ≤ 10
Reflections collected	3422
Independent reflections	1665 [R(int) = 0.0361]
Completeness to theta = 23.89°	89.4 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1665 / 0 / 145
Goodness-of-fit on F ²	1.075
Final R indices [I > 2σ(I)]	R1 = 0.0415, wR2 = 0.1051
R indices (all data)	R1 = 0.0442, wR2 = 0.1085
Largest diff. peak and hole	2.533 and -1.986 e.Å ⁻³

Table 2 Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for [PtCl₂(C₁₀H₉N₃)]. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U _{eq}
C(1)	11909(7)	6572(9)	5455(7)	47(2)
C(2)	11852(8)	5980(9)	4417(6)	49(2)
C(3)	10667(8)	5938(8)	3755(6)	48(2)
C(4)	9554(7)	6556(8)	4130(6)	41(2)
C(5)	9664(8)	7156(8)	5181(7)	37(2)
C(6)	8552(6)	8935(7)	6206(5)	34(2)
C(7)	7527(7)	9838(9)	6009(6)	45(2)
C(8)	7532(8)	10954(9)	6651(7)	50(2)
C(9)	8574(9)	11159(9)	7479(7)	54(2)
C(10)	9531(7)	10228(8)	7654(6)	42(2)
Cl(1)	10602(2)	8086(3)	9409(2)	52(1)
Cl(2)	12085(2)	5830(2)	8030(2)	54(1)
N(1)	10797(7)	7131(7)	5865(6)	35(2)
N(2)	9511(5)	9105(6)	7053(5)	34(1)
N(3)	8561(7)	7831(7)	5553(7)	42(2)
Pt(1)	10757(1)	7604(1)	7515(1)	33(1)

Table 3 Selected bond lengths [Å] and angles [°] for [PtCl₂(C₁₀H₉N₃)].

C(1)-C(2)	1.364(11)	C(1)-N(1)	1.368(10)
C(2)-C(3)	1.368(11)	C(3)-C(4)	1.379(11)
C(4)-C(5)	1.380(11)	C(5)-N(1)	1.338(10)

C(5)-N(3)	1.396(11)	C(6)-N(2)	1.342(8)
C(6)-N(3)	1.364(10)	C(6)-C(7)	1.382(10)
C(7)-C(8)	1.366(12)	C(8)-C(9)	1.388(12)
C(9)-C(10)	1.350(12)	C(10)-N(2)	1.346(10)
Cl(1)-Pt(1)	2.307(2)	Cl(2)-Pt(1)	2.296(2)
N(1)-Pt(1)	2.011(7)	N(2)-Pt(1)	2.020(6)
C(2)-C(1)-N(1)	121.5(7)	C(1)-C(2)-C(3)	120.2(7)
C(2)-C(3)-C(4)	119.0(7)	C(3)-C(4)-C(5)	118.7(7)
N(1)-C(5)-C(4)	122.6(8)	N(1)-C(5)-N(3)	118.0(7)
C(4)-C(5)-N(3)	119.3(7)	N(2)-C(6)-N(3)	119.5(6)
N(2)-C(6)-C(7)	121.1(7)	N(3)-C(6)-C(7)	119.3(6)
C(8)-C(7)-C(6)	119.2(7)	C(7)-C(8)-C(9)	119.2(7)
C(10)-C(9)-C(8)	119.1(8)	N(2)-C(10)-C(9)	122.3(7)
C(5)-N(1)-C(1)	117.8(7)	C(5)-N(1)-Pt(1)	120.1(6)
C(1)-N(1)-Pt(1)	121.2(5)	C(6)-N(2)-C(10)	119.0(6)
C(6)-N(2)-Pt(1)	119.5(5)	C(10)-N(2)-Pt(1)	121.1(5)
C(6)-N(3)-C(5)	128.5(7)	N(1)-Pt(1)-N(2)	88.7(3)
N(1)-Pt(1)-Cl(2)	90.8(2)	N(2)-Pt(1)-Cl(2)	177.22(16)
N(1)-Pt(1)-Cl(1)	176.9(2)	N(2)-Pt(1)-Cl(1)	90.88(17)
Cl(2)-Pt(1)-Cl(1)	89.48(8)		

Table 4 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{PtCl}_2(\text{C}_{10}\text{H}_9\text{N}_3)]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2hka^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	31(4)	58(6)	52(5)	-3(4)	4(3)	3(4)
C(2)	51(5)	52(5)	46(5)	-6(4)	19(4)	14(4)
C(3)	70(6)	41(5)	31(4)	-1(4)	6(4)	-9(4)
C(4)	42(4)	45(5)	34(4)	-8(4)	-2(3)	-3(4)
C(5)	32(5)	42(4)	36(5)	4(4)	-2(4)	-7(4)
C(6)	27(4)	45(5)	31(4)	-2(3)	2(3)	0(3)
C(7)	35(4)	61(6)	40(4)	11(4)	5(3)	9(4)
C(8)	51(5)	47(5)	54(5)	13(4)	15(4)	22(4)
C(9)	73(6)	37(5)	55(5)	5(4)	22(4)	3(5)
C(10)	39(4)	39(5)	45(4)	-5(4)	0(3)	0(4)
Cl(1)	43(1)	73(2)	39(1)	-11(1)	-9(1)	14(1)
Cl(2)	52(1)	57(1)	48(1)	-4(1)	-12(1)	21(1)
N(1)	35(4)	32(3)	38(4)	-2(3)	-4(3)	5(3)
N(2)	26(3)	38(4)	39(3)	-2(3)	4(2)	-1(3)
N(3)	24(4)	55(4)	47(4)	-13(4)	-4(3)	2(3)
Pt(1)	23(1)	40(1)	36(1)	-5(1)	-5(1)	1(1)

Table 5 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{PtCl}_2(\text{C}_{10}\text{H}_9\text{N}_3)]$.

	x	y	z	U(eq)
H(1)	12723	6596	5895	56
H(2)	12621	5603	4158	59
H(3)	10613	5499	3062	57
H(4)	8745	6569	3684	49
H(7)	6841	9688	5445	54
H(8)	6846	11568	6535	60
H(9)	8613	11926	7907	65
H(10)	10228	10369	8210	50
H(3A)	7786	7509	5342	51

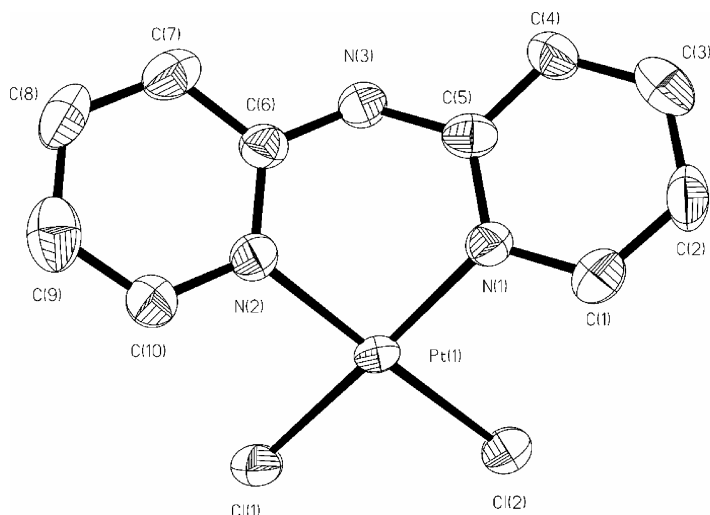


Fig. 2 Molecular structure of $[\text{PtCl}_2(2,2'\text{-dipyridylamine})]$ displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are not drawn.

Results and discussion

The compound $[\text{PtCl}_2(2,2'\text{-dipyridylamine})]$ is a mononuclear complex, which is shown in Fig.1. The central platinum atom has a square-planar geometry, which is coordinated by two chloride and two pyridyl nitrogen atoms in a cis fashion. The ligand 2,2'-dipyridylamine is potentially tridentate, but the NH group is not coordinated in the compound. The compound consists of a six-membered ring formed by 2,2'-dipyridylamine and the platinum atom. As can be seen from Table 2, the Pt-Cl bond distances [2.307(2) Å and 2.296(2) Å] and the Pt-N bond distances [2.011(7) Å and 2.020(6) Å] are all normal.

The Pt...Pt stacking is prevented due to large steric hindrance of 2,2'-dipyridylamine. The non-coordinated NH group and chloride involve in intermolecular hydrogen bonding interaction. The intermolecular N(3)...Cl(1) distance is 3.288(8) Å and the N-H...Cl angle is 167.9°.

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