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پژوهشی

تهیه و تعیین ساختار بلوری بیس(۲،٦-دی آمینوپیریدنیم) تتراکلروپالادات(II) ازیک سیستم خودمجموعه ساز شامل حلقه پیریدین

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چکیده : از واکنش بین لیگاند LH_2 (۲،٦ - پیریدین دی آمونیوم ۲،٦ - پیریدین دی کربوکسیلات) با پالادیم(II) کلرید کمپلکس بیس (۲،٦- دی آمینوپیریدنیم) تتراکلروپالادات (II) به دست می‌آید. ساختار بلوری این ترکیب به روش پراش سنجی پرتو X تعیین شد. بلورهای این ترکیب سه میل، با گروه فضایی $P\bar{1}$ و یک مولکول در یاختهٔ یکه است. ابعاد یاخته عبارتند از: c = ۱۲/۰۲۵(۳) Å ، b = ۷/۸۹۸(۳) Å ، a = ٦/۹۰۰(۳) Å

γ = ۹۲/٤۱۵(۱۲)° ، β = ۱۰٤/۰۸(۱٤)° ، α = ۱۰۳/۳۰۲(۱٤)°

پس ازتعیین ساختار مولکولی، مقدار R تا میزان ۰/۰٦۰۲ برای ۱۹۸۸ بازتاب کاهش یافت. تشکیل گونه‌های فرضی [pyda.H][Pd(pydc)(pydc.H)]، $[Pd(pydc.H)_2]$ و[pyda.H]Cl ، به وسیله طیف سنجی IR، ESI/MS، ^1H NMR، ^{13}C NMR و تجزیه عنصری مورد بررسی قرار گرفت.

واژه های کلیدی: پالادیم(II) کمپلکس، ساختار بلوری، سیستم خودمجموعه ساز.

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Crystal Structure of Bis (2,6-diaminopyridinium) tetrachloro palladate(II) of a Pyridine Containing Self-Assembling System

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Abstract: The reaction between LH_2, [pyda.H_2][pydc], (pyda = 2,6 – pyridinediamine and pydc. H_2 = 2,6 – pyridinedicarboxylic acid), ligand with palladium(II) chloride leads to the formation of [pyda.H]$_2$[$PdCl_4$]. The crystal system of the compound was determined by X–ray diffraction. The crystal system is triclinic with space group $P\bar{1}$ and one molecule per unit cell. The unit cell dimensions are a = 6.900(3) Å, b = 7.898(3) Å, c = 8.025 (3) Å, with α = 103.302(14)°, β = 104.068(14)° and γ = 92.415(12)°. The final R value is 0.0602 for 1988 reflections. The presumably of the formation [pyda.H][Pd(pydc)(pydc.H)], [Pd(pydc.H)$_2$] and [pyda.H]Cl species, was studied by IR, ESI/MS, ^{1}H NMR, ^{13}C NMR spectroscopy, and elemental analysis.

Introduction

The development of small organic components that can form self-assembling systems through non covalent interactions has been an active area of research over the past decade.[1] In continuing synthesis of metal complexes with novel self-assembling system LH_2,[2] we were interested to find out the influence of $[pyda.H_2]^{2+}$ cation in the complexation process of $PdCl_2$ with this ligand. Accordingly, we have succeeded, however, to make different mononuclear complexes {Cr(III), Cu(II), and Zn(II)}[3] possessing $[pyda.H]^+$, binuclear and polymer complexes {Pb(II), Cd(II) and Bi(III)}[4] without $[pyda.H]^+$ as a counter ion. The presumably of the formation of [pyda.H][Pd(pydc)(pydc.H)], $[Pd(pydc.H)_2]$ and [pyda.H]Cl species (Scheme 1). Here, we wish to report the X- ray crystal structure, IR, ESI/MS, ^1H NMR, ^{13}C NMR spectroscopy of a self-assembled Pd(II) complex, I, $[pyda.H]_2[PdCl_4]$.

A review on the literature showed that the [pydc.H2] or [pydc]2– form complexes by Pd(II) ion. The reaction of [Pd(acac)2] or [Pd(OAc)2]3 with [pydc.H2] in CH3CN affords [Pd(pydc)(NCMe)]. The reaction of this complex with PBu3, leads to the formation of [Pd(pydc)(PBu3)]2,5 for which the X–ray crystal structure has been reported.

Experiment

Preparation: To a solution of $PdCl_2$ (0.064g, 0.36mmol) in CH_3CN (100 ml) was added a solution of $\mathbf{LH_2}$ (0.2g, 0.72mmol) in CH_3CN (100 ml) and resulting light yellow brown solution refluxed for 48 hours, and concentrated with rotary evaporator. After two days at 5 ºC yellow crystals, accompanied by brown powder was obtained. After three times recrystallization in CH_3CN, we found suitable single crystals for X-ray diffraction. ^1H NMR, and ^{13}C NMR for powder (mixture) compounds (**I**, **II**, **III**): ^1H NMR (500 MHz, DMSO–d_6) δH 5.744 (d, 2H, H3,5 pyda.H(1)), 5.768 (d, 2H, H3,5 pyda.H(2)), 5.873 (d, 2H, H3,5 pyda.H(3)), 6.588 (br, s, NH_2 pyda.H(1)), 6.916 (br, s, NH_2 pyda.H(2)), 7.103 (br, s, NH_2 pyda.H(3)), 7.139 (t, 1H, H4, pyda.H(1)), 7.195 (t, 1H, H4, pyda.H(2)), 7.487 (t, 1H, H4, pyda.H(3)), 7.772 (d, 2H, H3,5 pydc(1)), 7.873 (d, 2H, H3,5 pydc(2)), 8.162 (m, 1H, H4, pydc(1)), 8.228 (d, 2H, H3,5 pydc(3)), 8.273 (t, H4, pydc(2)), 8.357 (t, H4, pydc(1)), 12.5 (br, 3H, NH, pyda.H(1, 2, 3)) ppm. ^{13}C NMR(500 MHz, DMSO–d_6) δC 95.543 (C3, pyda.H(3)), 96.205 (C3, pyda.H(2)), 97.047 (C3, pyda.H(1)), 128.017 (C3, pyda.H(1)), 128.139 (C3, pyda.H(2)), 128.187 (C3, pydc(3)), 139.755 (C4, pydc(1)), 140.483 (C4, pydc(2)), 140.968 (C4, pydc(3)), 141.171 (C4, pyda.H), 142.016 (C4, pyda.H), 142.874 (C4, pyda.H), 145.50 (C2, pyda.H), 148.67(C2, pyda.H), 148.789 (C2, pyda.H), 152.503 (C2, pydc), 157.943 (C2, pydc), 159.309 (C2, pydc), 166.001 (C5, pydc), 171.693 (C5, pydc), 171.837 (C5, pydc) ppm. ES/MS m/e (%) in HCOOH: 414.0 (0.12), 391.2 (0.57), 347.2 (0.12), 327.0 (0.55), 324.9 (1.12), 279.0 (0.23), 277 (0.26), 271.0 (0.37), 265 (0.35), 255 (0.96), 246.9 (0.14), 228.9 (0.15), 219.0 (1.29), 212 (0.27), 194.9 (0.12), 182.9 (1.33), 176.9 (0.39), 167.9 (0.14), 165.9 (0.2), 163.9 (0.93), 146.9 (8.30), 110.9 (0.21), 109.9 (21.29), 55.0 (54.42), 42.1 (100).

Results and Discussion

The reaction between LH_2 ligand with $PdCl_2$ leads to the formation of the crystalline product. The application of NMR spectroscopy on the resulting crystalline product, indicated the presence of three species involving (pyda.H). Based on the integration of ^1H NMR, the formation of $[pyda.H]_2[PdCl_4]$, $[Pd(pydc.H)_2]$, [pyda.H][Pd(pydc) (pydc.H)] and [pyda.H]Cl species were assumed. X-ray diffraction for the isolated yellow crystals from the crystalline crude product showed that the crystal system is triclinic with space group $P\bar{1}$ and one molecule per unit cell. The unit cell dimensions are a = 6.900(3) Å, b =7.898(3) Å, c = 8.025(3) Å, with α = 103.302(14)º, β = 104.068(14)º and γ = 92.415(12)º. The final R value is 0.0602 for 1988 reflections.

The X-ray data were collected by graphite–monochromated Mo-K_α radiation (λ=0.71073 Å). The crystal and experimental data are listed in Table 1. The bond distances and angles are given in Table 2. Lists of the collected data for atomic coordinates, anisotropic displacement parameters, hydrogen bonds and hydrogen coordinates for the complex I are given in the Tables 3-6 respectively. The structure was solved by direct methods using SHELXS-97 [6]. The non-hydrogen atoms were refined anisotropically by the full matrix least-square method. The hydrogen atoms were obtained from a difference Fourier map and some of the hydrogen atoms were included in the ideal position with fixed isotropic U values equal to 1.2 times that of the atom they are attached to. The numbering scheme and ORTEP view of the complex I is given in Fig. 1, while the unit cell packing diagram is illustrated in Fig 2. molecular structure of the title compound is shown in Fig.1 together with the atom-labeling scheme.

From the examination of the ORTEP plot of the complex I, it is evident that the resulting Pd(II) complex forms a crystal in which the Pd atom is in the center of a square-planar arrangement consisting of four chlorine donor atoms. The two Cl_2-Pd_1-Cl_{2A} and Cl_1-Pd_1-Cl_{1A} angles are 180.0º. The Cl_2-Pd_1-Cl_1 and Cl_{2A}-Pd_1-Cl_1 angles are 90.83º and 89.17º respectively. The Pd-Cl bond distances is in agreement with the previous reports such as $[PdCl_2(PN)]_2$, PN = P, N-bidentate aminophosphite ligands [7].

Table 1 Crystal and experimental data

Formula: $C_{10}H_{16}Cl_{14}N_6Pd$
Formula weight = 468.49
Temperature = 293(2) K
Crystal system: triclinic
Space group: $P\bar{1}$
Z = 1
a=6.900(3) Å α = 103.302(14)º
b=7.898(3) Å β = 104.068(14)º
c = 8.025 Å γ = 92.415(12)º
V = 410.6(3)$Å^3$
D_x = 1.895 g/cm^3
Absorption coefficient = 1.781mm^{-1}
F(0 0 0) = 232
Crystal dimensions (mm): 0.35× 0.20× 0.15
R = 0.0602, wR_2 = 0.1465
θ range for data collection: 2.66to 25.00º
Goodness-of-fit = 1.041
Largest diff. Peak and hole: 1.280and –1.260 e. $Å^{-3}$
No.of reflections used = 1331
No.of parameters = 117
Instrument: SHELXL-97
Measurement: Bruker SMART 1000 CCD
Program system: SMART V 5.051 and SAINT V 5.00
Structure determination: direct method
Refinement: full-matrix least-squares of F^2

An important feature of the crystal structure of the complex is the existence of an ionic form consisting of $PdCl_4^{2-}$ and two $[pyda.H]^+$ units. It worthy to note that, although we started the complexation reaction with a double protonated 2, 6-pyridinediamine and $[pydc]^{2-}$ salt, LH_2, the monocationic $[pyda.H]^+$ counter ion is generated, and there is no any $[pydc]^{2-}$ in the chemical structure of the Pd(II) complex. Hydrogen bonding and ion pairing play an important rule in the formation of a self-assembled Pd(II) complex. The hydrogen bonding takes place among the two components $[pyda.H]^+$ and $PdCl_4^{2-}$ (Table 6).

Table 2 Bond lengths (Å) and angles (º) for the complex I.

Pd(1)–Cl(2)	2.3107(19)	Cl(2)–Pd(1)–Cl(2)#1	180.00(9)
Pd(1)–Cl(2)#1	2.3107(19)	Cl(2)–Pd(1)–Cl(1)	90.83(6)
Pd(1)–Cl(1)	2.3122(16)	Cl(2)#1–Pd(1)–Cl(1)	89.17(6)
Pd(1)–Cl(1)#1	2.322(16)	Cl(2)–Pd(1)–Cl(1)#1	89.17(6)
N(1)–C(6)	1.356(9)	Cl(2)#1–Pd(1)–Cl(1)#1	90.83(6)
N(1)–C(2)	1.357(9)	Cl(1)–Pd(1)–Cl(1)#1	180.00(10)
C(2)–N(3)	1.341(9)	C(6)–N(1)–C(2)	125.4(6)
C(2)–C(3)	1.399(10)		
C(3)–C(4)	1.393(10)		
N(4)–C(6)	1.342(9)		
C(4)–C(5)	1.377(10)		
C(5)–C(6)	1.403(10)		

1 –*x*, –*y*, –*z*

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for the complex I. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	X	Y	Z	*U(eq)*
Pd(1)	0	0	0	17(1)
Cl(1)	2027(2)	119(2)	-1888(2)	21(1)
Cl(2)	147(2)	-2982(2)	-430(2)	19(1)
N(1)	6163(8)	4272(8)	-2629(7)	19(1)
C(2)	6163(10)	2835(9)	-3936(8)	19(1)
N(3)	7925(10)	2206(9)	-4000(9)	24(1)
C(3)	4334(10)	2165(10)	-5180(9)	23(2)
N(4)	4816(10)	6575(9)	-1110(8)	23(1)
C(4)	2624(9)	2975(9)	-4971(8)	20(2)
C(5)	2678(11)	4442(10)	-3637(9)	22(2)
C(6)	4538(10)	5129(9)	-2438(8)	19(2)

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for the complex I. The anisotropic displacement factor exponent takes the form: $2\pi^2[h^2a^{*2}U_{11}+...+2hka^*b^*U_{12}]$.

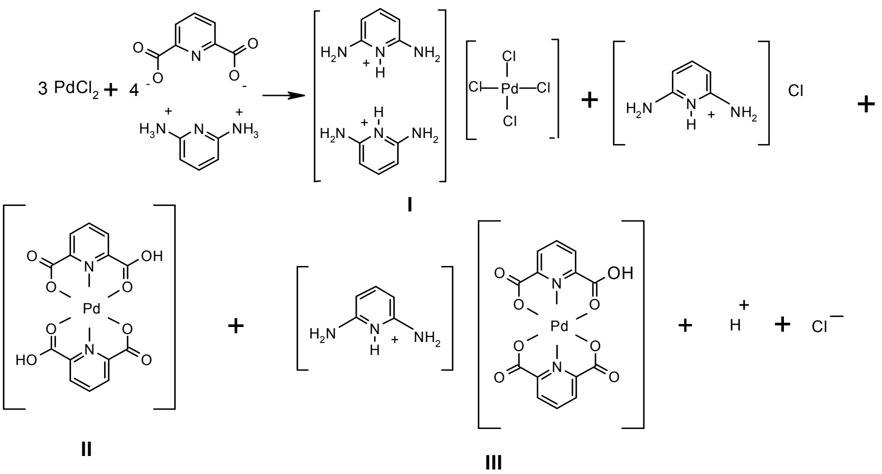
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd(1)	16(1)	10(1)	21(1)	-4(1)	3(1)	-4(1)
Cl(1)	21(1)	16(1)	24(1)	-5(1)	8(1)	-5(1)
Cl(2)	17(1)	10(1)	24(1)	-3(1)	2(1)	-4(1)
N(1)	15(3)	15(3)	21(3)	-5(2)	2(2)	-7(3)
C(2)	17(3)	12(4)	23(3)	-2(3)	4(3)	-4(3)
N(3)	18(3)	18(4)	29(3)	-8(3)	5(3)	0(3)
C(3)	24(4)	15(4)	25(3)	-1(3)	3(3)	-5(3)
N(4)	15(3)	16(3)	31(3)	-5(3)	5(3)	1(3)
C(4)	15(4)	22(3)	-5(3)	-1(3)	-9(3)	-9(3)
C(5)	23(3)	22(4)	22(3)	2(3)	10(3)	2(3)
C(6)	22(3)	13(4)	21(3)	-1(3)	9(3)	-4(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3).

Atom	**x**	**Y**	**Z**	***U(eq)***
H(1N)	7340(100)	4670(90)	-1850(80)	4(15)
H(3NB)	8820(180)	2360(150)	-3210(150)	60(40)
H(3NA)	7800(120)	1190(120)	-4840(110)	30(20)
H(3A)	4262	1204	-6123	28
H(4NB)	5890(150)	7050(120)	-650(110)	31(20)
H(4NA)	3880(130)	7310(120)	-1020(100)	30(20)
H(4A)	1395	2506	-5766	24
H(5A)	1514	4964	-3535	26

Table 6. Hydrogen bonds for the complex I.

D–H…A	**D–H (Å)**	**H…A (Å)**	**D…A (Å)**	**DHA [º]**	**A**
N1–H1N[*x*+1, *y*+1, *z*]	0.88(3)	2.48(3)	3.279(7)	150(2)	C12
N1–H1N[–*x*+1, –*y*, –*z*]	0.88(3)	2.81(3)	3.446(7)	130(2)	C12
N3–H3B [–*x*+1, –*y*, –*z*]	0.74(3)	2.74(3)	3.378(7)	144(2)	C12
N3–H3NA[–*x*+1, –*y*, –*z*–1]	0.87(3)	2.63(3)	3.397(7)	146(2)	C11
N4–H4NB[–*x*+1, –*y*+1, –*z*]	0.77(3)	2.72(3)	3.382(7)	144(2)	C11
N4–H4NB[*x*+1, *y*+1, *z*]	0.77(3)	2.91(3)	3.576(7)	145(2)	C12
N4–H4NA[*x*, *y*+1, *z*]	0.91(3)	2.73(3)	3.414(7)	133(2)	C12
N4–H4NA[*x*, *y*+1, *z*]	0.91(3)	2.74(3)	3.549(7)	149(2)	C11



Scheme 1. The reaction between [pyda.H2][pydc] and PdCl2.

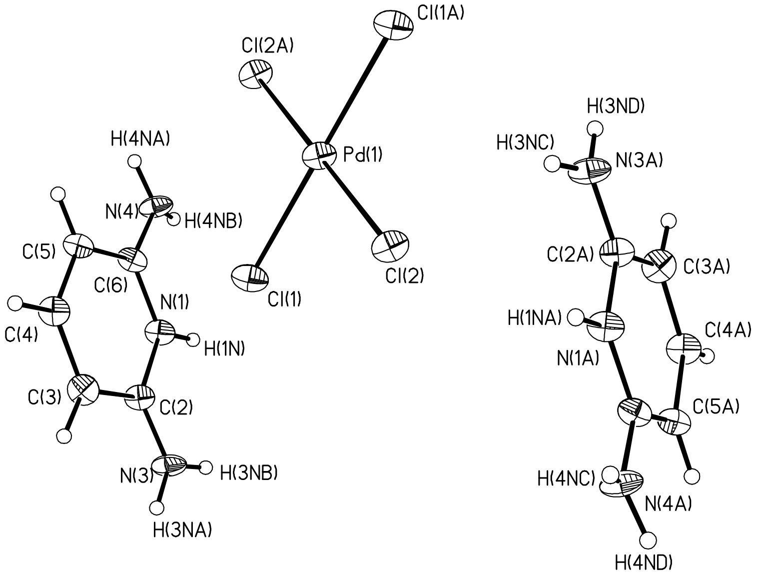


Fig 1. Molecular structure of the Pd(II) complex I with the atom labeling.

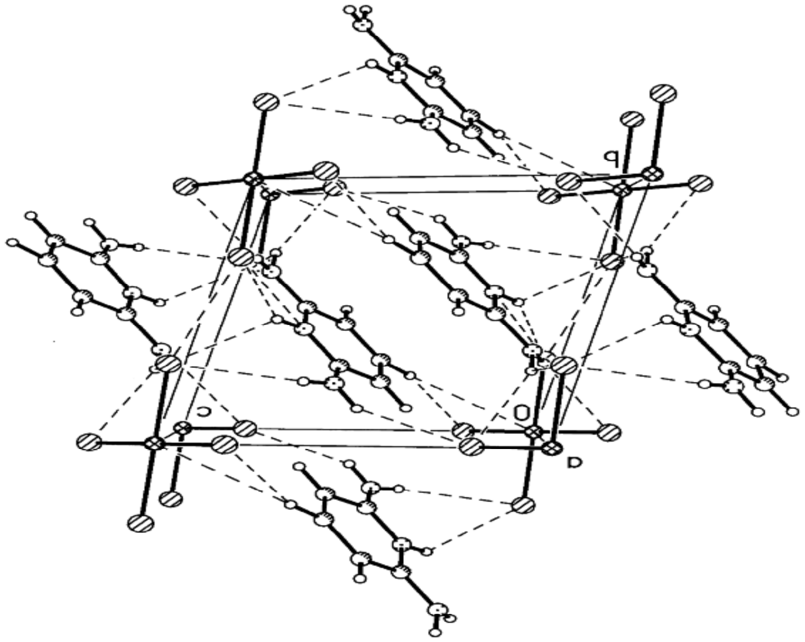


Fig. 2. Unit cell packing diagram of the Pd(II) complex I.

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