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Note

Diammine(pyrazine-2,3-dicarboxylato-*N,O*)palladium(II): synthesis, crystal structure, spectroscopic and thermal properties

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Abstract

The synthesis, crystal structure and spectroscopic (IR, XPS) characterization of a new Pd complex with 2,3-pyrazinedicarboxylic acid (2,3-H_2pzdc), Pd(2,3-pzdc)$(NH_3)_2$ (**1**), are reported. This compound crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. Using 2697 independent reflections up to $2\theta = 60°$, the structure was refined to $R = 0.044$. The lattice is formed of isolated zwitterionic moieties in which the square-planar coordination of palladium is ensured by three nitrogen atoms and one oxygen from a carboxylate group attached to the pyrazine ring. Both the structural and the infrared data confirm the absence of a polymeric network. Thermal degradation under nitrogen produces a mixture of palladium metal and PdO at 773 K. The XPS data of **1** are discussed together with those of a related compound with 3,5-pyrazoledicarboxylic acid (H_3Dcp), $(NBu_4)_2[Pd_2(Dcp)_2]$ (**2**) and suggest the presence of a delocalized positive charge in the pyrazine ring.

Keywords: Crystal structures; Palladium complexes; Pyrazinedicarboxylate complexes; Photoelectron spectroscopy

1. Introduction

Carboxylate-type compounds of transition metals generate great interest as potential precursors for the preparation of finely divided metal or oxide-type solid compounds, namely in fields like heterogeneous catalysis (pure or supported) and high-T_c superconductivity. In many of these applications, the absence of heteroatoms such as sulfur and halogens is a key point to prevent unwanted poisoning effects that alter the materials properties. Carboxylic derivatives of nitrogen-containing heterocycles behave ideally with respect to that point.

The present paper is dedicated to the synthesis, spectroscopic characterization and crystal structure determination of a new palladium coordination compound with 2,3-pyrazinedicarboxylic acid (2,3-H_2pzdc). This molecule is a rather strong acid ligand ($pK_{a1} = 0.8$, $pK_{a2} = 2.84$) with six potential coordination sites involving the oxygens of the carboxylic groups and the nitrogen atoms of the pyrazine ring. Several coordination types and three-dimensional arrangements were therefore observed [1–9], and in many cases, complexation results in the formation of infinite chains that give rise to collective magnetic properties, like ferromagnetic intrachain exchange in the complex Cu(2,3-pzdc)·HCl [10], or weak antiferromagnetic interactions in Co(2,3-Hpzdc)$_2$(H_2O)$_2$ [5]. In this work, the thermal behaviour of the title compound, in view of its use as a precursor for the incorporation of palladium in various materials, is also investigated. This approach is validated namely by the enormous catalytic potentialities of palladium, in reduction as well as in oxidation catalysis. Analogous Pd complexes described so far in the literature are the corresponding derivatives of 2,5-pyrazinedicarboxylic acid [11,12] (2,5-H_2pzdc) and 3,5-pyrazoledicarboxylic acid [13] (3,5-H_3Dcp). The crystal structure and spectroscopic characterization of the new palladium complex with 2,3-H_2pzdc will be described and compared with those reported for the complexes of other metals with similar ligands.

2. Experimental

2.1. Preparations

2.1.1. Pd(2,3-pzdc)$(NH_3)_2$ (1)

An ammoniacal suspension of palladium dichloride (Janssen 59 wt.% Pd, 250 ml, 0.01 mol) is added to a cold solution (160 ml) containing 0.01 mol of pyrazine-2,3-dicarboxylic acid (2,3-H_2pzdc, Janssen 97%). $PdCl_2$ dissolves on heating

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and the solution is concentrated upon boiling to about 200 ml. The compound Pd(2,3-pzdc)$(NH_3)_2$ (**1**) formed in the boiling mixture is collected on a sintered glass funnel without allowing the solution to cool down. The precipitate is washed with iced water and further dried in vacuo over P_2O_5 at 100°C (yield 55%). Yellow crystals of **1** grown from the filtrate upon standing at room temperature for several days are filtered and dried in air at room temperature.

Anal. Found: C, 23.45; N, 18.20; H, 2.55. Calc. for $C_6H_8N_4O_4Pd$: C, 23.49; N, 18.27; H, 2.61%. The palladium content was determined gravimetrically as the bis(dimethylglyoximato) complex $Pd(C_4H_7N_2O_2)_2$: found: 34.3; calc.: 34.7%.

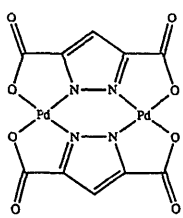
2.1.2. $(NBu_4)_2[Pd_2(Dcp)_2]$ (2)

The tetrabutylammonium salt of the dinuclear complex of palladium with 3,5-pyrazoledicarboxylic acid (Scheme 1) was synthesized according to a literature procedure [13].

2.2. Instrumental

2.2.1. Crystal structure determination

Suitable crystals of **1** were obtained by slow evaporation from water at room temperature. The crystals were examined at 20°C on a Huber four circle diffractometer with graphite monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å). Crystal measurement and refinement data are summarized in Table 1. The lattice parameters were refined using 19 reflections in the range $5° \leq 2\theta \leq 25°$. Intensities were collected with ω scans. One standard reflection was checked every 50 measurements and no significant deviation was observed. The intensity data were corrected for Lorentz polarization and for absorption by semi-empirical (ψ scans) method. The structure was solved from Patterson and difference syntheses using the programme SHELXL93 [14]. It was refined by full-matrix least-squares on F^2 with anisotropic temperature factors for all non hydrogen atoms. All the H atoms were localized from difference Fourier and included in the refinement with a common isotropic temperature factor ($U = 0.051$ Å^2). The largest peak in the final difference synthesis was close to the heavy atom. Atomic scattering factors were taken from Ref. [31]. Additional material available from the Cambridge Crystallographic Data Centre comprises full list of atomic coordinates, bond lengths and angles, H-atom coordinates, and thermal parameters.



Scheme 1.

Table 1
Data collection and refinement parameters

Formula	$C_6H_8N_4O_4Pd$
M_r	306.56
System	monoclinic
Space group	$P2_1/c$
a (Å)	8.348(2)
b (Å)	7.041(1)
c (Å)	15.875(4)
β (°)	97.89(2)
V (Å^3)	924.3(3)
Z	4
D_x (g cm^{-3})	2.203
λ (Å)	0.71069
$F(000)$	600
μ (mm^{-1})	2.009
Approximate crystal size (mm)	0.32×0.32×0.12
Collection range $(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.70
Range of h, k, l	$-8 \leq h \leq 11$ $-9 \leq k \leq 7$ $-22 \leq l \leq 22$
Indices of standard reflections	2 −1 −4
Number of collected reflections	5338
Number of independent reflections	2697 ($R_{int} = 0.037$)
Number of observed reflections ($I \geq 2\sigma(I)$)	2141
Number of parameters	161
Absorption corrections, min., max. transmission factors	0.8381, 1.1013
R ($I \geq 2\sigma I$)	0.0305
(all data)	0.0438
wR_2	0.0676
Weight	$1/[\sigma^2F_o^2 + 0.0353P^2]$
S	1.021
Extinction parameter	no correction
Shift/e.s.d. max.	0.003
Residual density (max., min.) (e Å^{-3})	0.610, −0.82

2.2.2. Physico-chemical characterization

Infrared spectra were registered as KBr pellets in the wavenumber range 4000–450 cm^{-1} on a Fourier Transform spectrometer Perkin-Elmer type 1710. Thermogravimetric analysis was carried out under air or nitrogen with a SETARAM TGC85 analyzer at a heating rate of 20 K min^{-1}. Powder X-ray diffractograms of the solid residues were obtained on a SIEMENS 500 diffractometer equipped with a copper anode.

X-ray photoelectron spectroscopy was performed on a SSI100 model 206 spectrometer from Surface Science Instruments. The binding energy scale was calibrated with respect to the C 1s photopeak of residual carbon fixed at 284.8 eV.

3. Results and discussion

3.1. Crystal structure

The molecular structure of complex **1** is illustrated in Fig. 1 and shows the square-planar coordination expected for

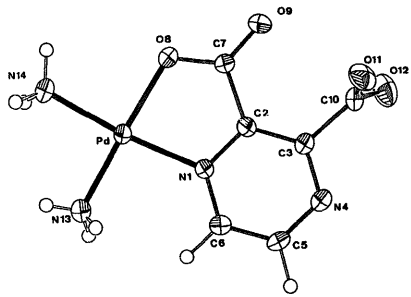


Fig. 1. Molecular structure of complex 1 with atom labelling [30].

palladium(II) compounds. The 2,3-pyrazinedicarboxylic acid ligand has six potential oxygen or nitrogen-based coordination sites. In the present case, metal coordination is ensured by three nitrogen atoms, two of them belonging to ammonia molecules, and the third one to the pyrazine ring, and by one oxygen atom from a carboxylate group. This type of coordination results in a five-membered ring around Pd, which is sterically much more favoured than the seven-membered ring that would be obtained if the two carboxylate groups in *ortho* positions were both acting as ligands for the same metal centre. The overall spatial configuration of complex 1 can be described by using three different planes. The first one contains the Pd atom and the four ligating atoms involved in its square planar coordination (O(8), N(1), N(13), N(14)). Mean deviations of these atoms from the mean plane are less than 0.04 Å and the metal atom is found to be located exactly (0.003 Å) within this plane. The second plane is that of the pyrazine ring and is slightly tilted, by some 10°, with respect to the first one. The third one is defined by the non-coordinating carboxylate group and is orientated at 75° from the second one. This orientation allows to minimize steric interactions between the oxygens of the two carboxylate groups, given the fact that the location of the oxygen atom O(9) is fixed by the involvement of O(8) in Pd coordination. The ionic nature of the second carboxylate is clearly demonstrated by the C(10)–O(12) and C(10)–O(11) bond distances, which are exactly the same (1.243(4) and 1.245(4) Å). The absence of hydrogen atom is confirmed by the lack of density in the neighbourhood of O(11) and O(12) atoms in the final Fourier difference synthesis. There is also no specific interaction between this carboxylic group and palladium atoms belonging to other molecules, as indicated by the Pd–O contact distances, the shortest ones ranging between 3.61 and 3.88 Å. In comparison with related complexes previously described in the literature [1–8], the present structure seems to be a rather uncommon example of coordination of 2,3-pyrazine dicarboxylate ligand, in the sense that a non-coordinating ionized carboxylate group is present and is not involved in a polymeric network, like that observed in Zn(II) and Co(II) complexes [4]. To the best of our knowledge, the only case where a deprotonated non-coordinating carboxylate group has been observed so far in such kinds of compounds is the Cu(II) complex with pyrazine-2,3,5,6-tetracarboxylic acid [9], in which the geometry (mean C–O value: 1.24 Å, O–C–O bond angle: 128°) is similar to that found in 1 (Table 2).

Table 2
Bond lengths (Å) and angles (°) for 1

Pd–N(1)	2.014(3)
Pd–N(14)	2.017(3)
Pd–O(8)	2.020(2)
Pd–N(13)	2.021(3)
N(1)–C(6)	1.333(4)
N(1)–C(2)	1.367(4)
C(2)–C(3)	1.378(4)
C(2)–C(7)	1.504(4)
C(3)–N(4)	1.349(4)
C(3)–C(10)	1.532(4)
N(4)–C(5)	1.345(5)
C(5)–C(6)	1.373(5)
C(7)–O(9)	1.221(4)
C(7)–O(8)	1.298(4)
C(10)–O(12)	1.243(4)
C(10)–O(11)	1.245(4)
N(1)–Pd–N(14)	173.9(1)
N(1)–Pd–O(8)	82.0(1)
N(14)–Pd–O(8)	92.2(1)
N(1)–Pd–N(13)	95.7(1)
N(14)–Pd–N(13)	90.1(1)
O(8)–Pd–N(13)	176.8(1)
C(6)–N(1)–C(2)	118.8(3)
C(6)–N(1)–Pd	128.9(2)
C(2)–N(1)–Pd	112.2(2)
N(1)–C(2)–C(3)	120.0(3)
N(1)–C(2)–C(7)	114.7(3)
C(3)–C(2)–C(7)	125.1(3)
N(4)–C(3)–C(2)	121.3(3)
N(4)–C(3)–C(10)	115.0(3)
C(2)–C(3)–C(10)	123.7(3)
C(5)–N(4)–C(3)	117.3(3)
N(4)–C(5)–C(6)	122.3(3)
N(1)–C(6)–C(5)	120.2(3)
O(9)–C(7)–O(8)	124.7(3)
O(9)–C(7)–C(2)	119.3(3)
O(8)–C(7)–C(2)	116.0(3)
C(7)–O(8)–Pd	114.1(2)
O(12)–C(10)–O(11)	126.5(3)
O(12)–C(10)–C(3)	116.6(3)
O(11)–C(10)–C(3)	116.8(3)

Except for a poorly reliable study published more than 20 years ago [15], there are no crystallographic data on the structure of the free ligand. The comparison is however possible with a compilation of numerous pyrazine [16] and carboxypyrazine [17–19] structures that are related to the present compound. In complex 1, the mean value of the C–C bond distances in the pyrazine ring (1.375 Å) is shorter than the average value reported in the literature (1.405 Å [16]). Similarly the C–N bond distances in 1 (mean value 1.348 Å) appear to be longer than in the other related compounds (1.336 Å [16]).

Table 3
Hydrogen bonding distances less than 3.0 Å in **1** (Å)

Hydrogen bond	N···O	H···O
N(13)–H(13A)···O(9) [a]	2.93	2.19
N(13)–H(13B)···O(12) [b]	2.95	2.06
N(13)–H(13C)···O(11) [c]	2.93	2.17
N(14)–H(14B)···O(12) [d]	2.93	2.09

Symmetry transformations
[a] $x, 0.5-y, 0.5+z$.
[b] $1-x, -y, -z$.
[c] $-x, -y, -z$.
[d] $x, -0.5-y, 0.5+z$.

The three Pd–N bonding distances are identical and similar to those observed in the tetraammine complex [12]. The departures observed for the bond angles within the square plane around Pd are in line with the involvement of N(1) and O(8) atoms in a five-membered ring (bond angle N(1)–Pd–O(8) equal to 82°) and with the steric hindrance between one ammonia ligand (N(13)) and the H atom bound to C(6) (bond angle N(1)–Pd–N(13) near 96°). The latter feature seems also to be responsible for the tilting angle of 10° between the plane of the pyrazine ring and that centered on the Pd atom. Similar angular deformations were reported in $Pd(en)Cl_2$ (bond angles Cl–Pd–Cl and N–Pd–N equal to 95.3 and 83.1°, respectively [20]). The steric interaction mentioned above is also assumed to produce the significant aperture of the C(6)–N(1)–Pd bonding angle up to 128.9(2)°.

The structural data related to the hydrogen bond network are listed in Table 3. This analysis was restricted to contact distances smaller than 3 Å and shows that the three hydrogen atoms of one ammonia molecule (N(13)) and one hydrogen bound to N(14) are involved in hydrogen bonds with oxygen atoms belonging to symmetric entities[1]. Fig. 2 illustrates the crystal packing. The isolated complexes are arranged in a head-to-tail fashion within a stacking of alternate parallel layers. Crystal cohesion is ensured by the hydrogen bonds in and between the stacked layers.

3.2. Infrared spectrum

The infrared spectrum of complex **1** shows strong carboxylate asymmetric stretching bands at 1672 and 1610 cm^{-1}. The first one is characteristic of carboxylate groups covalently bound to the metal atom, as reported in similar complexes previously described in the literature [1,2,7,8,11, 21,22]. The second band can be assigned to ionized unbounded carboxylate groups, as observed at about 1620 cm^{-1} in the sodium and potassium salts of the 2,3-pzdc ligand [2,21] and in the tetraammine complex $[Pd(NH_3)_4]$-(2,5-pzdc) [11]. The presence of this absorption band is also in line with the absence of a polymeric structure akin to that

[1] The two other hydrogen atoms bound to N(14) are distant from a symmetry related oxygen atom by ca 2.3 Å.

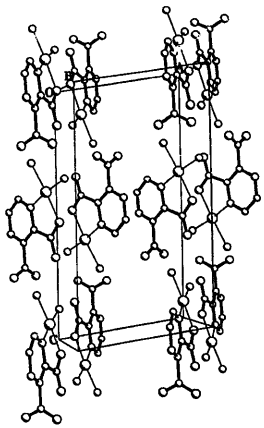


Fig. 2. View of the crystal packing in **1** [29].

observed in the analogous complexes of 2,3-dicarboxypyrazine with several metals of the first transition series [4]. The IR band centered at 1717 cm^{-1} in the spectrum of the free acid, assigned to stretching vibrations of the non ionized carboxylic group, is absent in the IR spectrum of the Pd(2,3-pzdc)$(NH_3)_2$ complex, confirming that the ligand is doubly ionized. Symmetric stretching bands of the carboxylate group appear at 1385 and 1318 cm^{-1}.

According to the literature [23,24], broad medium-strong bands at 3276 and 3202 cm^{-1} can be assigned to N–H stretching modes of the ammonia ligands, and the sharp band at 489 cm^{-1} corresponds most probably to a Pd–N stretching mode.

3.3. Thermal behaviour

The title compound is thermally stable in a nitrogen atmosphere up to ca. 573 K, then undergoes degradation in essentially one step. A similar behaviour has been observed in several 2,3-pyrazinedicarboxylate complexes of the first transition series [1,7], which were all found to decompose into the corresponding metal oxides. At 773 K, the residue corresponds to a total weight loss of ca. 60%. Theoretical weight losses for Pd metal and PdO are 65 and 59.4%, respectively. The experimental result suggests that the compound is converted into a Pd–PdO mixture, as checked by X-ray powder diffractometry of the TGA residue.

3.4. Photoelectron spectra

The binding energy values of carbon (C 1s), oxygen (O 1s), nitrogen (N 1s) and palladium (Pd $3d_{5/2}$) in the complexes **1** and **2** and the related free ligands are listed in Table 4.

Table 4
XPS data of the complexes $Pd(2,3\text{-pzdc})(NH_3)_2$, $(NBu_4)_2[Pd_2(Dcp)_2]$ and the corresponding free ligands $2,3\text{-}H_2pzdc$ and $H_3Dcp \cdot H_2O$

Photopeak		Binding energy (eV) (Relative intensities, %)				Assignment
		$Pd(2,3\text{-pzdc})(NH_3)_2$ **1**	$2,3\text{-}H_2pzdc$	$(NBu_4)_2[Pd_2(3,5\text{-Dcp})_2]$ **2**	$3,5\text{-}H_3Dcp$	
C 1s	(I)	284.8 (21)	284.8 (8)	284.8 (72)	284.8 (28)	CH_x
	(II)	286.3 (53)	286.3 (63)	286.0 (20)	285.9 (38)	C=N
	(III)	288.6 (26)	289.4 (29)	288.2 (8)	289.2 (34)	COO
O 1s		531.4 (100)	532.2 (60)–533.7 (40)	531.0 (100)	531.9 (52)–533.3 (48)	COO
N 1s	(I)		400.1 (100)		400.0 (50)	N=C
	(II)				401.3 (50)	N–H
	(I)	399.5 (25)–400.1 (50)		400.3 (68)		N–Pd
	(II)	401.1 (25)		401.9 (32)		N^+, NBu_4^+
Pd $3d_{5/2}$		338.8 (100)		338.5 (100)		Pd^{2+}

All the C 1s photoelectron spectra of the palladium compounds **1** (Fig. 3(a)) and **2** (Fig. 3(c)) and the corresponding free ligands exhibit three components. The first one at the lowest energy (C(I)) corresponds to the residual hydrocarbonaceous 'CH_x' contamination. For each compound, this component was fixed at 284.8 eV as reference value for the binding energy scale. The highest energy component (C(III)) corresponds to the carboxylic group and, in both Pd complexes, is shifted downwards (0.8 eV in **1**, 1.0 eV in **2**) in the carboxylate group. The intermediate component (C(II)) can be assigned to the heterocyclic carbon bound to nitrogen and, as expected, is not affected by the formation of the complex. In agreement with the stoichiometric bulk composition, the intensity ratios C(II)/C(III) are close to 2.0 in **1**.

The C 1s spectrum of compound **2** (Fig. (3(c)) shows the same general shape. In this case, the C(I) component includes also the C4 atom of the pyrazole ring and three of the four aliphatic carbons of the butyl chains, whereas C(II) is the sum of all nitrogen-bound carbon atoms, i.e. heterocyclic carbon (C3, C5) and the remaining carbon of the butyl groups. The experimental intensity ratio of the C 1s components in **2** (C(I):C(II):C(III) equal to 2.0:5.0:17.5) is in agreement with the theoretical value of 2:6:13 if one takes into account the additional contribution of residual contamination to C(I).

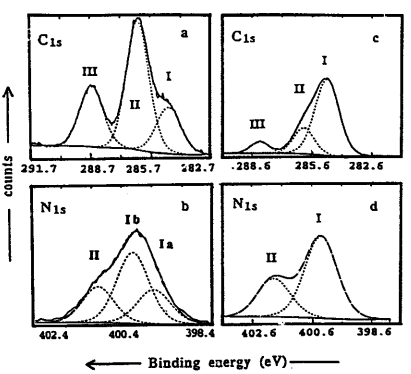


Fig. 3. C 1s and N 1s photoelectron spectra of $Pd(2,3\text{-pzdc})(NH_3)_2$ (**1**) (a, b) and $(NBu_4)_2[Pd_2(Dcp)_2]$ (**2**) (c, d).

In both complexes, the Pd 3d photoelectron spectra attest the presence of Pd(II). Furthermore, ionization of the two carboxylic groups removes the non equivalence between the oxygen atoms and the O 1s photoelectron spectra of both compounds display one single oxygen photopeak.

The N 1s photoelectron spectrum of complex **1** (Fig. 3(b)) shows three components with an intensity ratio equal to 2:1:1. The assignment of these components was made by comparing with the data obtained on compound **2** and by referring to the literature [25–28]. The two lowest energy components in complex **1**, labelled N(Ia) and N(Ib) can be identified as nitrogen atoms bound to palladium; in agreement with their relative intensities, they are assumed to correspond to nitrogen atoms belonging to the pyrazine ring and the ammonia ligands, respectively. Literature values for the *cis*- and *trans*-diammine complexes $Pd(NH_3)_2X_2$ (X=Cl, Br) and the tetraammine complex $[Pd(NH_3)_4]X_2$ lie in the range 400.2–400.5 eV [27] and the value of 400.2 eV has been reported in the Pd complex with 2-pyridinecarboxylic acid [25]. The third component in the N 1s spectrum of complex **1** is characterized by a higher binding energy and approaches the value observed for the nitrogens of the tetrabutylammonium cations in **2** (Literature value for NBu_4^+ is 401.7 eV [28]); this shift is therefore assumed to reveal the presence of a delocalized positive charge in the pyrazine ring, in relationship with the zwitterionic nature deduced from the crystallographic data.

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