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Synthesis and characterization of N-benzoyl-DL-α-valinato complexes of palladium(II), platinum(II). Crystal structure of a complex with deprotonated nitrogen coordinating to the palladium(II)

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Abstract—Reactions of $MLCl_2$ (M = Pd(II), Pt(II); L = bipy, phen) with Bzval H_2 (Bzval H_2 = N-benzoyl-DL-α-valine) in aqueous solution at pH ~9 gave three complexes [Pd(bipy)(Bzval-N,O)] (**1**), [Pd(phen)(Bzval-N, O)]·H_2O(**2**) and [Pt(bipy)(Bzval-N,O)]·H_2O(**3**). All of these complexes were characterized by elemental analysis and IR spectra. The structure of **1** has been determined by X-ray diffraction analysis. In all complexes an N-benzoyl-DL-α-valinate dianion coordinates to the metal ion through a deprotonated amide nitrogen and a carboxylic oxygen. There is some intramolecular interaction between phenyl ring and bipy in the complex. © 1997 Elsevier Science Ltd

Keywords: N-benzoyl-DL-α-valine; deprotonated amide; crystal structure; 'O'-like; intramolecular interaction; palladium.

The coordination behaviour of RCON-amino acids might be expected to show some similarities to that of the O-terminal end of peptides and proteins and great attention has been paid to the coordination properties of these ligands [1–3]. Although there are three potential donor sites, *viz*, carboxylic oxygen, amide oxygen, nitrogen, in all complexes reported before 1989 only the carboxylic oxygen has been involved in coordination. Appleton *et al.* reported the results of an investigation of the reactions of *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ with N-acetylglycine; they obtained the first reported complex in which N-acetylglycine acts as an N,O-chelating ligand [4]. A complex in which N-benzoylglycine acts as an N,O-chelating ligand also has been reported [5]. Until now however, no X-ray structural evidence for RCON-amino acids coordinating to a metal ion through a deprotonated amide nitrogen and carboxylic oxygen has been published, although several examples of RSO_2N-amino acids binding through deprotonated sulfonamide nitrogen and carboxylic oxygen have been reported [5–7]. As knowledge of metal ion interaction with the amide group will provide insight into protein structure and functional pathways in biological systems, herein we report reactions of $M(bipy)Cl_2$ [M = Pd(II), Pt(II)] with N-benzoyl-DL-α-valine in aqueous solution at pH ~9 gave complexes with deprotonated nitrogen, and the structure of one complex has also been reported.

EXPERIMENTAL

Materials

All chemicals were reagent grade and used without further purification. N-benzoyl-DL-α-valine was synthesized according to the procedure previously

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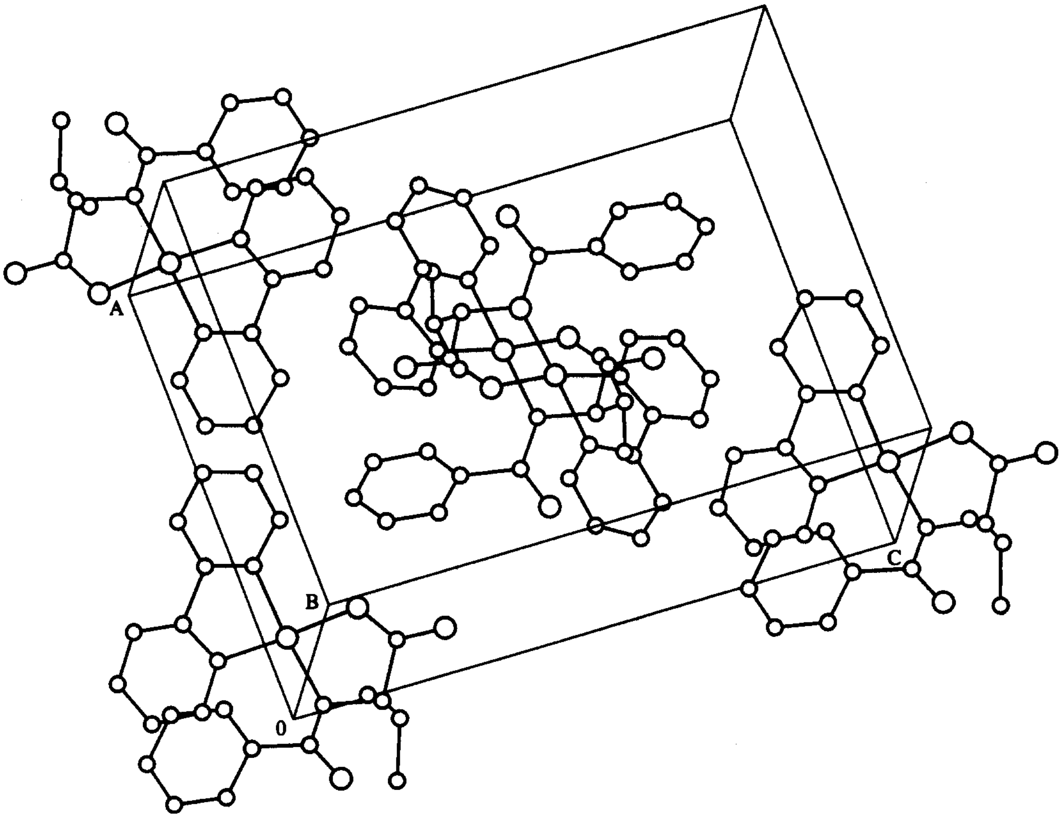

described [8] and characterized by elemental analysis and IR spectra. Pd(bipy)Cl$_2$, Pd(Phen)Cl$_2$ and Pt (bipy)Cl$_2$ were synthesized as literature [9–10] and characterized by elemental analysis.

Preparation of complexes

[Pd(bipy)(Bzval-N,O)](**1**) and [Pd(phen)(Bzval-N,O)] · H$_2$O(**2**). Pd(bipy)Cl$_2$ or Pd(phen)Cl$_2$ (1 mmol) was added to 30 cm^3 of aqueous solution containing N-benzoyl-DL-α-valine (442 mg, 2 mmol) at pH ~12 with rapid stirring. The pH dropped and it was corrected to ~9 with KOH continually. Filtered the solution until the solid Pd(bipy)Cl$_2$ or Pd(phen)Cl$_2$ almost disappeared, then heated the solution for a moment and concentrated it to about 80% of the original volume. Complexes separated from the solution after several days. Complex (**1**). Yield 70%. Found: C, 54.8; H, 4.5; N, 8.9. Calc. For C$_{22}$H$_{21}$N$_3$O$_3$Pd: C, 54.8; H, 4.4; N, 8.7%. Complex (**2**). Yield 60%. Found: C, 55.2; H, 4.5; N, 8.1. Calc. for C$_{24}$H$_{23}$N$_3$O$_4$Pd: C, 55.0; H, 4.4; N, 8.0%.

*[Pt(bipy)(Bzval-*N,O)] · H$_2$O(**3**). Pt(bipy)Cl$_2$ (1 mmol) was added to 30 cm^3 of aqueous solution containing N-benzoyl-DL-α-valine (442 mg, 2 mmol) at pH ~12 under fast stirring, then refluxed the mixture. The pH dropped and it was corrected to ~9 with KOH continually. Cooled and filtered the solution until the solid Pt(bipy)Cl$_2$ almost disappeared. After several days the yellow complex precipitated. Yield 60%. Found: C, 45.2; H, 4.0; N, 7.1. Calc. for C$_{22}$H$_{23}$N$_3$O$_4$Pt: C, 44.9; H, 3.9; N, 7.1%.

Instrumental equipment

The elemental analysis was performed on Carlo Erba 1106. The IR spectra were recorded with a Perkin–Elmer 683 spectrophotometer in the 4000–200 cm^{-1} region using KBr disks.

Crystallography

A crystal of **1**, dimensions 0.48 × 0.33 × 0.30 mm, was used for X-ray data collection on an Enraf-Nonius CAD4 diffractometer operating in the $\omega/2\theta$ scan mode. Within the range $2 < 2\theta < 50°$, 3069 independent reflections were obtained at 20°C, and 1614 observed reflections with $I > 3\sigma(I)$ were used in the further calculations. An empirical absorption correction was applied [11]. Crystallographic data are listed in Table 1. The structure was solved by the heavy-atom method from the experimental Patterson function and refined by full-matrix least-squares analysis. Non-hydrogen atoms were refined anisotropically, hydrogen atoms placed at their geometrically calculated position; the temperature factors of hydrogen atoms were not refined. The final

Table 1. Crystallographic data for complex 1

Formula	$C_{22}H_{21}N_3O_3Pd$
Colour	Orange–yellow
Crystal system	Monoclinic
space group	$P2_1/n$
a (Å)	11.758(2)
b (Å)	10.960(1)
c (Å)	15.937(5)
β (°)	92.54(2)
V (Å^3)	2051.9(9)
Z	4
μ (mm^{-1})	0.918
Radiation, λ (Å)	Mo–K_α 0.71073
D_c (g cm^{-3})	1.566
(Δ/σ) max	0.03
(Δ/e) min, max (e Å^{-3})	−0.354, 0.281

discrepancy factors were $R = \Sigma||F_0|-|F_c||\Sigma|F_0| = 0.0209$ and $R_w = [\Sigma W(|F_0|-|F_c|)^2/\Sigma W|F_0|^2]^{1/2} = 0.0318$. All calculations were performed on a DEC Microvax II computer using SDP V5.0.

RESULTS AND DISCUSSION

The method of formation is notable, it appears that N-benzoyl amino acid can substituate chlorine ion and coordinate to Pd(II) or Pt(II) through the deprotonated amide nitrogen and the carboxylic oxygen under suitable condition. The reaction may show some similarities to reaction of the anticancer drug *cis*-$Pt(NH_3)_2Cl_2$ with peptides and proteins.

IR spectra

The most important IR spectra of $BzvalH_2$ and complexes are listed in Table 2. The lack of ν(NH) (amide) indicates the amide group being deprontonated and coordinates to metal ion through nitrogen, it is also confirmed by the amide I shifting from 1640 cm^{-1} to 1554 (1550) cm^{-1} and disappearance of amide II from its original region. The values of ν_{as}(OCO), ν_s(OCO) and $\Delta\nu$ [$\nu(OCO)_{as}-\nu(OCO)_s$] indicate that carboxylate group coordinates to metal ion as monodentate.

Description of the structure

The structure of complex **1** is shown in Fig. 1, selected bonds and angles are listed in Table 3. Figure 1 shows that the 2,2′-bipyridyl, the carboxylic oxygen, and the deprotonated amide nitrogen coordinate to the slightly distorted square-planar positions of Pd(II). The four atoms of the chelating group O(1)—C(11)—C(19)—N(3) show deviations from their mean plane ranging from −0.052 to 0.045 Å, with the Pd atom 0.664 Å out of the plane. The Pd—N (deprotonated amide) [1.971(3) Å] bond is shorter than the Pd—N(2,2′-bipyridine) [2.013(3), 2.023(4) Å] distances, consistent with the deprotonated amide nitrogen being a better σ donor [12]. On the other hand, the Pd—N (deprotonated amide) bond is similar to Pd—O (carboxylic [1.987(4) Å], showing that Sigel's surmise [13], that the coordinating qualities of the deprotonated amide nitrogen are 'O-like' as the deprotonated amide group is isoelectronic with the carboxylate group is reasonable.

There appears to be some intramolecular interaction between the phenyl ring and bipy (Table 4). The edge of one bipyring, containing N(2)—C(10)—C(9), is near to the phenyl ring, distances from C(10) to all atoms of phenyl ring is less than 3.9 Å, the shortest (C(10)···C(17)) is 3.114(6) Å which is significantly smaller than the sum of appropriate van der Waals radii. The dihedral angle between the plane of bipy and phenyl ring is 41.78 (±0.12)°, this result shows aromatic moieties do not necessarily have to be coplanar for an interaction; i.e., intramolecular interactions are possible in other orientations.

Table 2. Infrared spectra of ligand and complexes

Compounds	ν(NH),amide	Amide I	Amide II	ν_{as}(OCO)	ν_s(OCO)	$\Delta\nu$
$BzvalH_2$	3392(sh)	1640(vs)	1546(vs)	1745(vs)	1211(vs)	534
Complex 1	—	1554(vs)	—	1645(vs)	1405(vs)	240
Complex 2	—	1550(vs)	—	1650(vs)	1406(vs)	244
Complex 3	—	1550(vs)	—	1670(vs)	1397(vs)	273

Table 3. Selected bond lengths (Å) and angles (°) for complex 1

Pd—N(1)	2.013(3)	Pd—N(2)	2.023(4)	Pd—N(3)	1.971(3)
Pd—O(1)	1.987(4)	N(3)—C(18)	1.355(4)	O(3)—C(18)	1.245(4)
N(1)—Pd—N(2)	79.6(1)	N(2)—Pd—N(3)	104.0(1)	O(1)—Pd—N(1)	94.7(1)
O(1)—Pd—N(3)	82.0(2)	O(3)—C(18)—N(3)	124.8(3)	O(3)—C(18)—C(17)	118.5(3)
N(3)—C(18)—C(17)	116.6(3)				

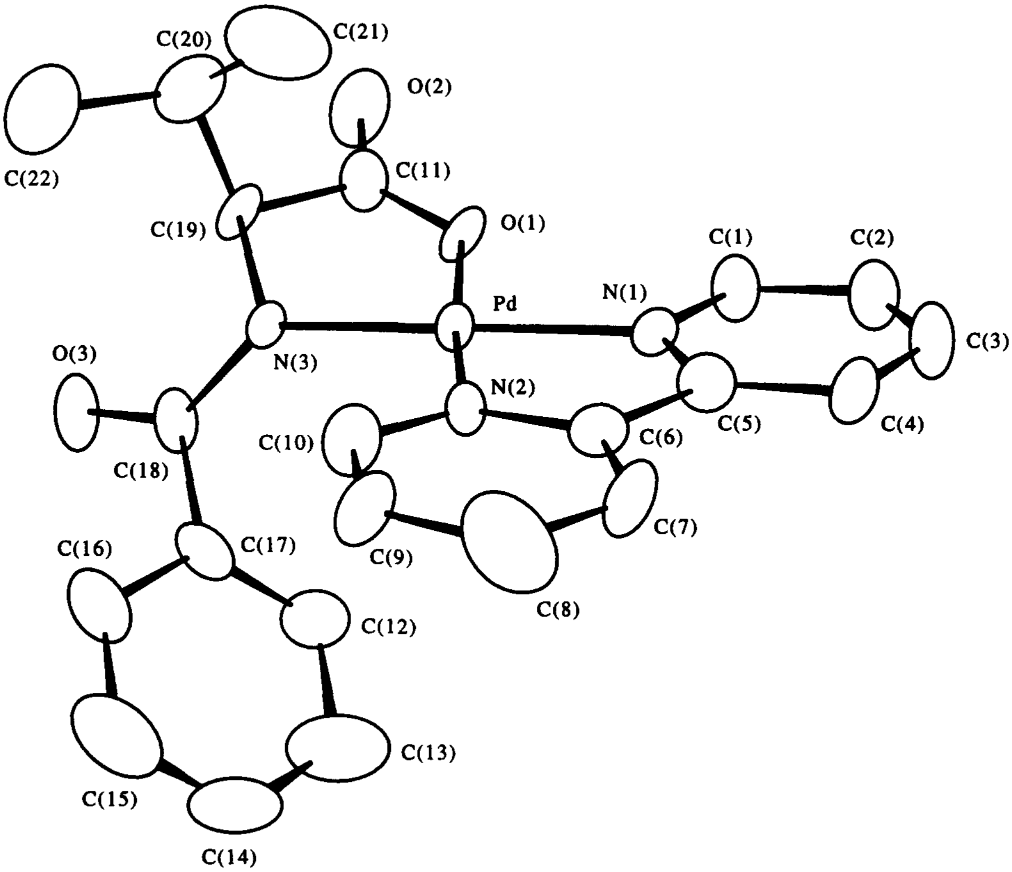

Fig. 1. Molecular structure of [Pd(bipy)(Bzval-N,O)].

Table 4. Intramolecular interaction between phenyl ring and bipy (distance in Å)

N(1)···C(12)	3.250(4)	N(2)···C(13)	3.803(4)	N(2)···C(17)	3.405(5)
C(10)···C(12)	3.320(5)	C(10)···C(13)	3.704(5)	C(10)···C(14)	3.868(5)
C(10)···C(15)	3.709(5)	C(10)···C(16)	3.348(5)	C(10)···C(17)	3.114(6)
C(9)···C(14)	3.970(5)	C(9)···C(15)	3.885(6)	C(9)···C(16)	3.955(7)

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