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CRYSTAL AND MOLECULAR STRUCTURE OF A NEW PALLADIUM(II) COMPLEX WITH A COUMARIN-VALINE DERIVATE

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The new coumarine derivate with methyl ester of 2-((*Z*)-1(2,4-dioxochroman-3-ylidene)ethyl-amino)-3-methylbutanoic acid and the corresponding palladium(II) complex are synthesized and characterized by microanalysis, infrared, ^{1}H and ^{13}C NMR spectroscopy. The proposed structure of the ligand was confirmed based on the X-ray structural study.

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K e y w o r d s: coumarine-derived ligand, palladium(II) complex, crystal structure.

INTRODUCTION

Coumarins and their derivatives are widely spread in nature, especially in the world of plants, although they are also found in the metabolites of microorganisms and animals [1]. Coumarine derivatives have spasmolytic, antiarrhythmic, cardiotonic, and photodynamic properties [2], as well as antioxidant [3] and antitumor activity [4]. Metal complexes with coumarine derivatives are also used in significant anticoagulant [5, 6] and antitumor activity [2, 7] investigations. Some researchers showed that cerium(III), zirconium(IV), copper(II), zinc(II), bismuth(III), and cadmium(II) were significantly cytotoxic *in vitro* [8, 9].

The initial results of antitumor testing of palladium complexes, due to their structural analogy with platinum(II) complexes, were not very encouraging. The palladium(II) complexes generally showed a lower antitumor activity than cisplatin. This could be explained due to a more labile nature of the palladium(II) complexes in comparison to the corresponding platinum(II) complexes [10]. However, some palladium(II) complexes exerted a higher antitumor activity in comparison to cisplatin and carboplatin. Budzisz et al. found that the palladium(II) complex with 4-hydroxy-3-(1-iminoethyl)-2*H*-chromen-2-one was 7800 times more active than carboplatin [11].

The rapid emergence of pan-resistant bacterial strains is a major medical problem throughout the world. Some resistant strains have developed mechanisms of resistance to all existing antibiotics. The great number of newly synthesized ligands and their metal(II) complexes have been screened for their

antimicrobial activities. The antibacterial screening has demonstrated that copper(II) and silver(I) complexes have the greatest and broad activities among the investigated complexes [12—14]. A wide range of biochemical processes may be responsible for the action mechanism of free ligands and their metal(II) complexes against different microorganisms [15].

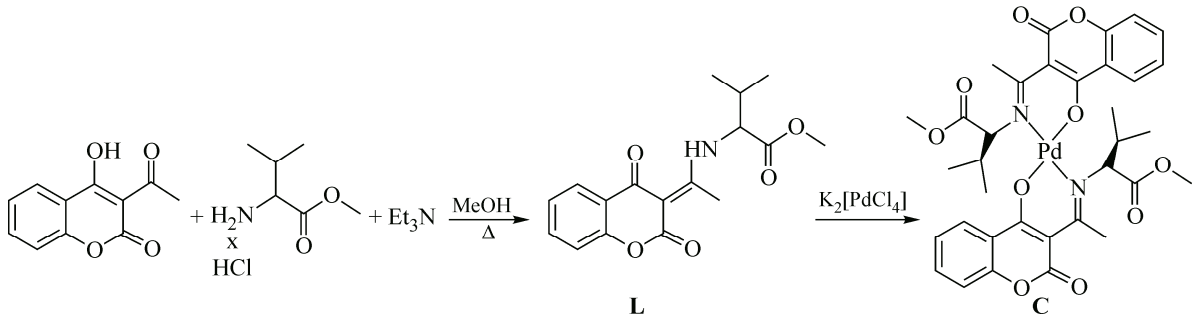
Herein we described the synthesis and characterization of the new coumarine derivate with methyl ester of amino acid *S*-valine, methyl 2-(1-(2,4-dioxochroman-3-ylidene)ethylamino)-3-methylbutanoate and the corresponding palladium(II) complex. The crystal structure of methyl 2-(1-(2,4-dioxochroman-3-ylidene)ethylamino)-3-methylbutanoate is also described.

EXPERIMENTAL

Materials and methods. *S*-Valine methyl ester hydrochloride, triethylamine, methanol, ethanol, toluene, acetone and potassium tetrachloridopaladate(II) were obtained from Sigma Aldrich, Germany. The 3-acetyl 4-hydroxy-coumarine compound was synthesized by the previously described procedure [11].

Elemental microanalyses for C, H, and N were performed by the standard methods on a Vario EL *III* C, H, N Elemental Analyzer. The melting point of the ligand was determined using a Kofler-hot stage apparatus and was uncorrected. Infrared spectra were measured on a Perkin-Elmer Spectrum One FT-IR spectrometer by the KBr pellet technique (4000—400 cm^{-1}). The NMR spectra were recorded on a Varian Gemini 200 spectrometer (Varian, Palo Alto, CA); ^{1}H NMR at 200 MHz and ^{13}C NMR at 50 MHz, solvent DMSO-d_6, TMS internal standard. The chemical shifts were given in δ (ppm) and coupling constants (*J*) in Herz (Hz) (abbreviations: s — singlet, d — doublet, dd — doublet of doublet, m — multiplet, br s — broadend singlet). Mass spectra were recorded on a 5973 mass spectrometer (Agilent, Santa Clara, CA) (MS quadruple temperature 150 °C; mass scan range, 40—600 amu at 70 eV). Analytical TLC was performed on silicagel (Silica gel 60, layer 0.20 mm, Alugram Sil G, Mashery-Nagel, Germany). The visualization of TLC plates was performed using an UV lamp at 254 nm and 365 nm (VL-4.LC, 365/254, Vilber Lourmat, France).

Synthesis of methyl 2-(1-(2,4-dioxochroman-3-ylidene)ethylamino)-3-methylbutanoate, L. A mixture of 3-acetyl 4-hydroxy coumarine (0.400 g, 0.002 mol), *S*-valine methyl ester hydrochloride (0.335 g, 0.002 mol), and trimethylamine (0.202 g, 0.002 mol) in methanol (50 ml) was refluxed for 2 h. The progress of the reaction was monitored by TLC (toluene:acetone = 8:2). After the completion of the reaction the solvent was evaporated to half of its volume. Upon the addition of 5 ml of water, the obtained white crystals were filtered, dried, and recrystallized from 96 % ethanol. Yield: 0.53 g (83 %) (Scheme 1).



Scheme 1. Preparation of methyl 2-(1-(2,4-dioxochroman-3-ylidene)ethylamino)-3-methylbutanoate **L** and *bis*(methyl 2-(1-(2,4-dioxochroman-3-ylidene)ethylamino)-3-methylbutanoate)-palladium(II) complex **C**

Chemical formula: $C_{17}H_{19}NO_5$, MW: 317.34, Elemental analysis: calcd: C 64.34, H 6.03, N 4.41, found C 64.34, H 6.03, N 4.41. M.p. 182—184 °C. IR (KBr) ν, cm^{-1}: 3467 and 3210 (NH), 3030 (=CH), 2969 and 2850 (CH), 1743 (C=O from $COOCH_3$), 1706 (C=O from 2,4-dioxochroman part), 1609, 1571, 1487 and 1467 (C=C), 1138 (C—O—C from $COOCH_3$). ^{1}H NMR (DMSO-d_6, 200 MHz): δ (ppm) 1.69 (6H, d, $^{3}J_{H^{3''},H^{2''};H^{4''},H^{2''}}$ = 6.3 Hz, $CH^{3''}$; $CH^{4''}$), 1.97 (1H, m, $CH^{2''}$), 2.70 (3H, s,

$C^{1'}CH_3$), 3.84 (3H, s, $COOCH_3$), 4.62 (1H, m, C—$H^{1''}$), 7.25 (2H, m, CH^6, CH^7), 7.53 (1H, dd, $^3J_{H^8,H^7}$ = 7.96 Hz, $^4J_{H^8,H^6}$ = 2.71 Hz, CH^8), 8.07 (1H, dd, $^3J_{H^5,H^6}$ = 8.14 Hz, $^4J_{H^5,H^7}$ = 1.99 Hz, C—H^5), 12.62 (0.18 H, bs, NH) and 14.74 (0.82H, bs, NH) from two isomers. ^{13}C NMR (DMSO-d_6, 50 MHz): δ (ppm) 18.70 ($C^{1'}CH_3$), 18.92 ($C^{3''}$, $C^{4''}$), 42.35 ($C^{2''}$), 52.48 ($C^{1''}$), 53.10 ($COOCH_3$), 98.87 (C^3), 116.46 (C^8), 123.51 (C^6), 126.05 (C^5), 128.95 (C^{10}), 133.94 (C^7), 153.09 (C^9), 165.94 (C^2), 170.59 (CH_3OOC), 176.01 ($C^{1'}$) and 182.64 (C^4).

Synthesis of palladium(II) complexes, C. Potassium tetrachloridopalladate(II) (0.0500 g, $1.53 \cdot 10^{-4}$ mol) was dissolved in 10 ml of water on a steam bath and the double amount of methyl 2-(1-(2,4-dioxochroman-3-ylidene)ethylamino)-3-methylbutanoate (0.0971 g, $3 \cdot 10^{-4}$ mol) dissolved in methanol (10 ml) was added. The mixture was stirred for 3 h and the yellow precipitate was obtained. The precipitate was filtered off. Yield: 0.056 g (49.6 %) (Scheme 1).

Chemical formula: $C_{34}H_{36}N_2O_{10}Pd$, MW: 739.05, Elemental analysis: Calcd: C 55.25, H 4.91, N 3.79, found C 55.89, H 4.82, N 3.68. IR (KBr) ν, cm^{-1}: 3011 (=CH), 2958, 2925 and 2851 (CH), 1742 (C=O from COOCH3), 1708 (C=O from coumarine), 1606 (C=N), 1570, 1543 and 1486 (C=C), 1138 (C—O—C from $COOCH_3$), 526 (Pd—O), 463 (Pd—N). ^{1}H NMR (DMSO-d_6, 200 MHz): δ (ppm) 1.60 (6H, d, $^3J_{H^{3''},H^{2''};H^{4''},H^{2''}}$ = 6.01 Hz, $CH^{3''}$; $CH^{4''}$), 2.35 (1H, m, $CH^{2''}$), 2.62 (3H, s, $C^{1'}CH_3$), 3.76 (3H, s, $COOCH_3$), 4.91 (1H, m, $CH^{1''}$), 7.30 (2H, m, CH^6, CH^7), 7.66 (1H, m, CH^8), 7.99 (1H, dd, $^3J_{H^5,H^6}$ = 8.00 Hz, $^4J_{H^5,H^7}$ = 2.00 Hz, CH^5). ^{13}C NMR (DMSO-d_6, 50 MHz): δ (ppm) 17.42 ($C^{1'}CH_3$), 18.75 ($C^{3''}$, $C^{4''}$), 31.13 ($C^{2''}$), 52.67 ($C^{1''}$), 53.17 ($COOCH_3$), 96.78 (C^3), 116.36 (C^8), 120.28 (C^6), 123.80 (C^5), 125.76 (C^{10}), 134.30 (C^7), 152.87 (C^9), 161.72 (C^2), 169.87 (CH_3OOC), 177.08 ($C^{1'}$) and 180.60 (C^4).

X-ray data collection and structure refinement. A summary of the X-ray diffraction experiment and structure refinement for **L** is given in Table 1. The data collection for **L** was performed on an

Table 1

Crystal data and structure refinement of 2-(1-(2,4-*dioxochroman*-3-*ylidene*)*ethylamino*)-3-*methylbutanoate* **L**

Compound	**L**
Empirical formula	$C_{17}H_{19}NO_5$
Formula weight	317.33
Temperature, K	173(2)
Wavelength, Å	0.71073
Crystal system; space group	Monoclinic; $P2_1$
Unit cell dimensions: a, b, c, Å; β, deg.	5.1467(2), 12.9904(5), 11.8223(5); 96.644(4)
Volume, Å^3	785.10(5)
Z; D_c, g·cm^{-3}	2; 1.342
Absorption coefficient, mm^{-1}	0.099
F(000)	336
Crystal shape; color	Prism; colorless
Crystal size; mm	0.406×0.189×0.091
θ range for data collection, deg.	3.136—26.493
Index ranges	$-6 \le h \le 6$, $-16 \le k \le 16$, $-14 \le l \le 14$
Reflections collected / independent	6596 / 3260 [R(int) = 0.0240]
Data / restraints / parameters	3260 / 1 / 213
Goodness-of-fit on F^2	1.015
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0385, $wR2$ = 0.0773
R indices (all data)	$R1$ = 0.0528, $wR2$ = 0.0842
Absolute structure parameter	0.6(5)
Extinction coefficient	0.013(4)
Largest diff. peak and hole, e/Å^3	0.151 and –0.144

Oxford Diffraction Xcalibur 2 diffractometer equipped with a Sapphire2 CCD detector with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). Crysalis CCD [16] was used for data collection while Crysalis RED [16] was used for cell refinement, data reduction, and absorption correction. The structure was solved by SUPERFLIP [17] and subsequent Fourier syntheses using SHELXL2013 [18], implemented in the WinGX program suit [19]. Anisotropic displacement parameters were refined for all non-hydrogen atoms. The hydrogen atoms of aromatic carbon atoms, methyl, methine, and amine groups were placed in the calculated positions and refined riding on their parent C or N atoms with C—H or N—H distances of 0.95 Å, 0.98 Å, 1.00 Å, and 0.88 Å, respectively with U_{iso}(H) = = 1.2, U_{eq}(C,N). The analysis of bond distances and angles was performed using SHELXL2013; DIAMOND [20] was used for molecular graphics.

Computational study. Geometry optimizations were performed with the Gaussian 09 package [21]. All structures were optimized using the B3LYP functional. The SDD basis set for all atoms was employed in the calculations. All systems were optimized without symmetry restrictions. The resulting geometries were characterized as equilibrium structures by the analysis of the force constants of normal vibrations. Supplementary data associated with the quantum chemical calculations can be obtained from the authors upon request.

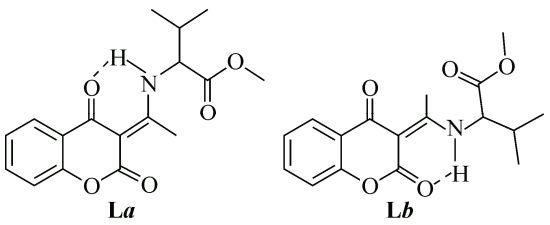
RESULTS AND DISCUSSION

Chemistry. The ligand **L** as well as the corresponding palladium(II) complex **C** were synthesized as depicted in Scheme 1. The treatment of equimolar amounts of 3-acetyl 4-hydroxy coumarine and *S*-valine methyl ester hydrochloride in the presence of triethylamine in refluxing methanol yielded the ligand **L**. The palladium(II) complex **C** was synthesized by mixing **L** and potassium tetrachloridopalladate(II) in a 2:1 molar ratio in a water/methanol (1:1, v/v) solution at room temperature for 3 h.

The structure of the compound **L** was confirmed by spectroscopic methods (IR, ^{1}H NMR, ^{13}C NMR, and MS) as well as by elemental analysis. The IR spectra showed characteristic bands at 3467 cm^{-1} and 3210 cm^{-1} for the NH group, 1743 cm^{-1} for the carbonyl group from COOCH3 and 1706 cm^{-1} for the carbonyl group from the 2,4-dioxochroman part. In the ^{1}H NMR spectrum of the ligand **L**, the signals of 2,4-dioxochroman protons (four aromatic protons) appeared at 7.25 ppm (multiplets from CH6 and CH7), 7.53 ppm (doublet of doublet from CH8), and 8.07 ppm (doublet of doublet from CH5), respectively. Methyl protons from the carbon atom attached to C1′ in a form of a singlet showed a resonance at 2.70 ppm, while the singlet from $COOCH_3$ was observed at 3.87 ppm. Proton magnetic resonance of the NH group at 12.62 ppm and 14.74 ppm, indicated that the compound **L** exists in a $CHCl_3$ solution in two forms. Based on the ratio of integrals (0.82:0.18), a more stable isomer **L*a*** (the structure with a hydrogen bond between the NH proton and the C4 carbonyl group) showed a resonance of the NH proton at 14.74 ppm in contrast to the isomer **L*b*** (the structure with a hydrogen bond between the NH proton and the C2 carbonyl group) (Fig. 1).

In the ^{13}C NMR spectra, C1′ carbon atom was observed at 176.01 ppm, whereas the methyl carbon atom attached to C1′ was noted at 18.70 ppm. Two carbonyl groups from the 2,4-dioxochroman moiety, lactone and ketone, were noticed at 165.94 ppm and 182.64 ppm, respectively. Six aromatic carbon atoms showed resonances at 116.46 ppm (C8), 123.51 ppm (C6), 126.05 ppm (C5), 128.95 ppm (C10), 133.94 ppm (C7), and 153.09 ppm (C9), while the C3 carbon atom was observed at 98.87 ppm. Carbonyl from the methyl ester group, as well as the carbon atom from the position C1″, appeared at chemical shifts at 170.59 ppm and 52.48 ppm, respectively. The base peak in MS spectra at 258 *m*/*z* corresponds to the M^-—$COOCH_3$ fragment ion.

The IR spectral data of the obtained palladium(II) complex **C** exhibited significant differences in comparison to the ligand **L**. The observed stretching vibration of the enamino NH group in the ligand **L** was not present in the complex **C**. Also, the bands at 1606 cm^{-1}



L*a* **L*b***

Fig. 1. Structure of **L*a*** and **L*b*** isomers

T a b l e 2

Characteristic group in the IR spectra and their wavenumbers

Compound	ν, cm^{-1}				
	NH	C=O	C=N	Pd—O	Pd—N
L	3467 and 3210	1706	/	/	/
C	/	1708	1606	526	463

T a b l e 3

Differences of characteristic chemical shifts in the ligand **L** *and the corresponding palladium*(II) *complex* **C**

1H NMR (200 MHz) δ, ppm		
Compound		δ, ppm
L (DMSO-d_6)	**C** (DMSO-d_6)	
2.70 (s, 3H, $CH_3C^{1'}$)	2.62 (s, 3H, $CH_3C^{1'}$)	–0.08
4.62 (m, 2H, $CH_2C^{2''}$)	4.91 (m, 2H, $CH_2C^{2''}$)	0.29
1.97 (m, 1H, $CHC^{1''}$)	2.35 (m, 1H, $CHC^{1''}$)	0.38
14.74 and 12.62 (br s, 1H, NH)	/	/

and 463 cm^{-1} belonging to the C=N and Pd—N groups, respectively, indicate that the nitrogen atom is involved in the coordination (Table 2). The presence of a Pd—O band at 526 cm^{-1} and the identified coumarine lactone band at 1708 cm^{-1} indicated that the formation of the Pd complex caused a transformation of the enamine ligand into the imino form.

The ^{1}H NMR spectra of the palladium(II) complex **C** show no broadened singlets at 14.74 ppm and 12.62 ppm from the NH group of the enamine ligand part. The protons from the methyl group attached to C-1′ show a resonance at 2.62 ppm, being 0.08 ppm lower than that in the ligand **L**. However, multiplets from CH2 protons from C-1″ and CH protons from C-2″ were observed at higher frequencies (4.91 ppm and 2.35 ppm, respectively) (Table 3).

Structure description. The crystal structure of **L** (Fig. 2) indicates that the compound occurs in a keto-amine tautomeric form in the solid state, stabilized by an intramolecular N1—H1…O3=C4

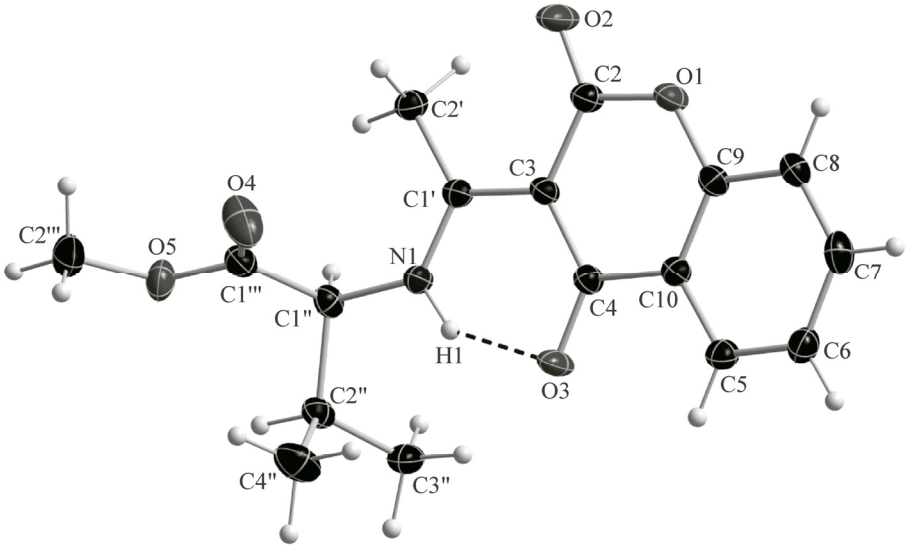


Fig. 2. Crystal structure of **L** (displacement ellipsoids are drawn at 40 % probability, intramolecular hydrogen bond is shown as dashed line)

Table 4

Hydrogen bonds for **L** (Å) *and angles* (deg.)

D—H…A	*d*(D—H)	*d*(H…A)	*d*(D…A)	∠(DHA)
N1—H1…O3	0.88	1.77	2.529(3)	142.9
C2‴—H2B…O2^{i}	0.98	2.52	3.394(4)	148.0
C3″—H3″B…O3^{ii}	0.98	2.41	3.325(4)	154.6

Symmetry transformations used to generate equivalent atoms: ^{i} –*x*–1, *y*+1/2, –*z*; ^{ii} *x*–1, *y*, *z*.

hydrogen bond, confirming the dominance of the more stable **L*a*** isomer in the solution, and conjugated by a double-bond system. Considering the O3=C4—C3=C1′—N1—H1 fragment, we can observe the equalization of the C3—C4 (1.434(4) Å) and C3=C1′ (1.437(4) Å) bond lengths although the bonds are formally single and double, respectively. The exocyclic C3=C1′ double bond has an *E* geometry, obviously due to the effect of the above mentioned hydrogen bond. We also observed the elongation and shortening of the C4=O3 (1.259(3) Å) and C1′—N1 (1.321(3) Å) bonds, respectively. The same bond lengths (within 3σ) were observed in the related 3-[(1-benzylamino)ethylidene]-2*H*-chromene-2,4(3H)-dione compound [23]. However, in the similar 3-(1-((2-hydroxyphenyl)amino)ethylidene)-2*H*-chromene-2,4(3*H*)-dione compound [24] the equivalence of the C3—C4 (1.437(3) Å) and C3=C1′ (1.429(3) Å) bond lengths was not fully achieved although all the other above discussed bond lengths are equal (within 3σ) to the corresponding bonds in **L**. The π-electron delocalization effect in **L** is strong due to the planarity and aromatic character of the coumarin part of the molecule (the largest deviation from the mean plane being 0.029(2) Å for the O2 atom). Moreover, due to the π-electron delocalization, not only the coumarin-ring system is essentially planar but an atomic ensemble involving coumarin rings along with the C2″—C1″—N1—C1′—C2′ fragment is also essentially planar, as indicated by the maximum deviation of 0.114(3) Å at the C1″ atom. All the other bond lengths and angles in the molecule of **L** are within normal ranges [25].

The **L** molecule itself is stabilized by the intramolecular N1—H1…O3 hydrogen bond forming a cyclic *S*6 motif [26] (Table 4). The molecular packing is governed by intermolecular C—H…O hydrogen bonds and π—π stacking interactions. The C2‴—H2B…O2^{i} hydrogen bond producing a C10 chain motif [26] links the molecules to form an infinite *zig-zag* chain along the *b* axis (Fig. 3) being

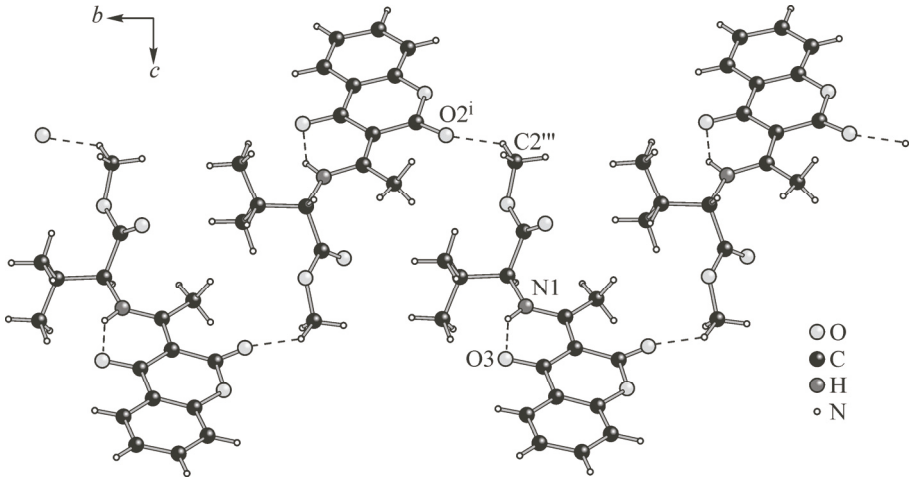


Fig. 3. Part of the chain formed in the structure of **L** (intramolecular and intermolecular hydrogen bonds are shown as dashed lines).
[Symmetry code: (i) = –*x*–1, *y*+1/2, –*z*]

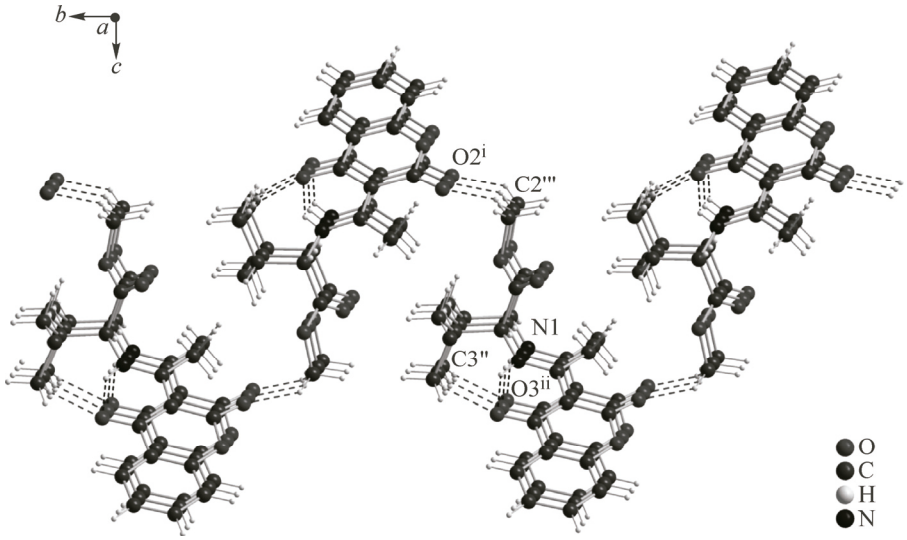


Fig. 4. Part of the wave-like plane formed in the structure of **L** (intramolecular and intermolecular hydrogen bonds are shown as dashed lines).
[Symmetry codes: (i) = –*x*–1, *y*+1/2, –*z*; (ii) = *x*–1, *y*, *z*]

further tied to the neighboring chain by the C3″—H3″B…O3^{ii} hydrogen bond (producing a C9 chain motif [26]) to form a wave-like plane in the *ab* plane (Fig. 4). The next stabilization of the so formed plane comes from face to face π—π interactions [27] between the phenyl and pyran-2,4-dione rings from coumarin rings in two adjacent chains, as evidenced by distances between the ring centroids (Cg) (3.716(2) Å) and by the angle between the phenyl ring normal and the vector connecting ring centroids (23.2°). Finally, the structure is also stabilized by C—H…Cg (π-ring) interactions involving C2′—H2′B and the pyran-2,4-dione ring (with a H2′B…Cg distance of 2.77 Å and C2′—H2′B…Cg angle of 125°).

Quantum chemical calculations. Structural isomers **L*a*** and **L*b*** were investigated by DFT calculations. **L*a*** appears to be energetically more favorable being 1.93 kcal/mol more energetically stable than **L*b***. The results are within the error of DFT calculations, but are in accordance to the finding from NMR spectroscopy stating that the **L*a*** isomer is found much more abundant than **L*b***. In the reaction of the ligand precursor methyl-2-(1-(2,4-dioxochroman-3-ylidene)ethylamino)-3-methylbutanoate with $K_2[PdCl_4]$ two isomers might be obtained: *cis* and *trans* arranged k^2-N,O ligands. In order to determine which of the two isomers is formed, chemical calculations were employed.

The structures were fully optimized without any symmetry constraints and were found to represent the equilibrium structures. The calculated results for the *bis*(methyl-2-(1-(2,4-dioxochroman-3-ylidene)ethylamino)-3-methylbutanoate)palladium(II) complex showed that the *trans* isomer appeared to be structurally and synthetically feasible. The energy differences between *trans*- and *cis*-*bis*(methyl-2-(1-(2,4-dioxochroman-3-ylidene)ethylamino)-3-methylbutanoate) palladium(II) isomers is 11.2 kcal/mol. DFT calculations are in agreement with the results of the NMR spectroscopy (within the sensitivity limits of the NMR spectroscopy) where the presence of only one isomer is observed. Thus, the DFT calculations indicate that the isolated isomer could be assigned to *trans*-bis(methyl-2-(1-(2,4-dioxochroman-3-ylidene)ethylamino)-3-methylbutanoate) palladium(II).

CONCLUSIONS

Methyl 2-(1-(2,4-dioxochroman-3-ylidene)ethylamino)-3-methylbutanoate crystallized in the monoclinic crystal system with the $P2_1$ space group. The crystal structure is dominantly stabilized by the intramolecular N—H…O3=C4 hydrogen bond. Based on the DFT calculation, the *trans* geometry to the corresponding Pd(II) complex with methyl 2-(1-(2,4-dioxochroman-3-ylidene)ethylamino)-3-methylbutanoate can be assigned.

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CCDC 1062329 contains the supplementary crystallographic data for **L**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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