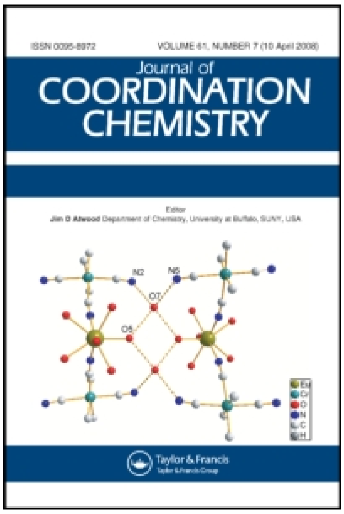

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Coordination ability of 3-pyridinyl coumarins with palladium(II) and platinum(II)

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Coordination ability of 3-pyridinyl coumarins with palladium(II) and platinum(II)

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The coordination ability of two 3-pyridinyl coumarins with Pd(II) and Pt(II) both in solution and in solid state is elucidated by conventional and linear-polarized IR-spectroscopy of oriented colloid suspensions in nematic liquid crystal, ^{1}H- and ^{13}C-NMR, UV-Vis spectroscopy, positive and negative ion mass spectrometry (ESI), HPLC tandem mass spectrometry (HPLC ESI MS/MS), TGV, and DSC methods. The four metal complexes are compared with free ligands. Density functional theory calculations are performed to obtain the electronic structure and vibrational properties of the compounds to support the experimental data.

Keywords: 3-Pyridinyl-coumarins; Benzopyran; Complexes; Pd(II) and Pt(II); Structure and spectroscopic properties

1. Introduction

Coumarins have been intensively studied due to their wide biological activity. Spasmolytic, antiarhythmic, cardiothonic, antiviral, and anticancer properties have been proposed and observed in some derivatives [1, 2]. The anticancer effect of some Pt(II) complexes with coumarins and pyridines has been used in therapy. Tuning the cytotoxic effect of the complexes with ligands containing both coumarin and pyridine could occur. As part of our systematic study on the synthesis [3–7], spectroscopic, and structural characterization of coumarins [8–10], their salts and metal complexes with potential biological activity [1–5], we report four new Pd(II) and Pt(II) complexes of 3-pyridin-2-yl (**1**) and 3-pyridin-3-yl (**2**) 2H-chromen-2-ones (scheme 1). Investigation with metal ions is based on similar behavior and coordination ability with Pt(II) toward N- and O-containing ligands [11]. The complexes were characterized by a variety of techniques and compared with the free ligands.

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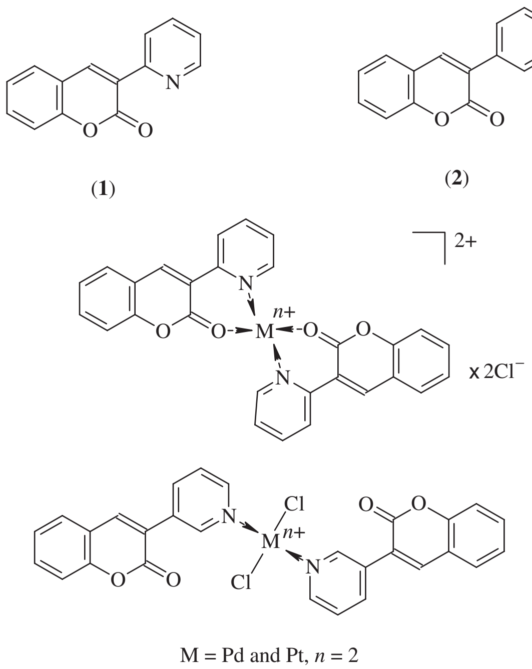


Scheme 1. Diagram of the 3-pyridinyl coumarins (**1**) and (**2**) and their coordination with Pt(II) and Pd(II).

2. Experimental

2.1. *Methods*

Conventional and polarized IR-spectra were measured on a Thermo Nicolet OMNIC FTIR-spectrometer (4000–400 cm^{-1}, 2 cm^{-1} resolution, 200 scans) equipped with a Specac wire-grid polarizer. The far IR-spectra are recorded on a Perkin–Elmer FTIR 1720 spectrometer as CsI pellets. Nonpolarized solid-state IR spectra were recorded using KBr disks. Oriented samples were obtained as a colloid suspension in a nematic liquid crystal ZLI 1695. The theoretical approach, experimental technique for preparing the samples, procedures for polarized IR-spectra interpretation and validation of this new linear-dichroic infrared (IR-LD) orientation solid-state method for accuracy and precision has been presented. The influence of the liquid crystal medium on peak positions and absorbances of the guest molecule bands, the rheological model, the nature and balance of the forces in the nematic liquid crystal suspension system, and morphology of the suspended particles have also been discussed [12–15].

The *positive and negative ESI mass spectra* were recorded on a Fisons VG autospect instrument employing 3-nitrobenzylalcohol (Sigma-Aldrich) as the matrix. Analyses of the purity of the samples by *HPLC-ESI MS/MS* were performed with a Thermo Finnigan surveyor LC-Pump. Compounds were separated on a Luna C18 column ($150 \times 2\,\mathrm{mm}^2$, 4 μm particle size) from Phenomenex (Torrance, CA, USA). The mobile phase consisted of water + 0.1% HCOOH (A) and acetonitrile + 0.1% HCOOH (B) using a gradient program presented in table 1. The compound was detected via UV and a TSQ 7000 (Thermo Electron Corporation, Dreieich, Germany) mass spectrometer.

Table 1. HPLC ESI MS/MS conditions.

n	*t* (min)	A (%)	B (%)	Rate ($\mu L\,min^{-1}$)
0	0.00	100	0	200
1	3.00	100	0	200
2	8.00	65	35	200
3	9.00	0	100	200
4	14.00	0	100	200
5	14.50	100	0	200
6	20.00	100	0	200

Ultraviolet (*UV*) *spectra* were recorded on a Specord UV-Vis (Carl Zeiss-Jena) using water and 0.0921 cm quartz cells.

The *thermal analyses* were performed in the 300–500 K region on a Differential Scanning Calorimeter Perkin–Elmer DSC-7 and a Differential Thermal Analyzer DTA/TG (Seiko Instrument, model TG/DTA 300). The experiments were carried out at a scanning rate of $10\,K\,min^{-1}$ under argon.

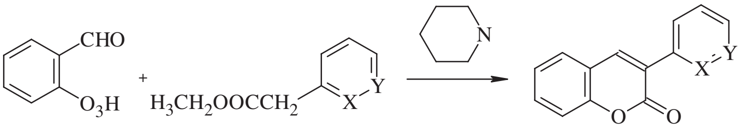
Elemental analyses were carried out according to the standard procedures for C and H (as CO_2 and H_2O) and N (by the Dumas method).

The ^{1}H- and ^{13}C-NMR measurements were performed at 298 K with a Bruker DRX-600 spectrometer using 5 mm tubes and D_2O as solvent. The chemical shift reference was sodium 3-(trimethylsilyl)tetradeuteriopropionate.

Quantum chemical calculations were performed with the GAUSSIAN 98 and Dalton 2.0 program packages [16, 17]. The geometries of **1** and **2** were optimized at density functional theory (DFT) using the 6-311++G** basis set. The DFT method employed is B3LYP, which combines Backe's three-parameter, nonlocal exchange functional with the correlation functional of Lee, Yang, and Parr. Molecular geometries were fully optimized by the force gradient method using Bernys' algorithm. For every structure, stationary points found on the molecule potential energy hypersurfaces were characterized using standard analytical harmonic vibrational analysis. The absence of imaginary frequencies, as well as negative eigenvalues of the second-derivative matrix, confirmed that the stationary points correspond to a minima of the potential energy hypersurfaces. The calculated vibrational frequencies and infrared intensities were checked to establish which calculations agreed best with the experimental data (section 3). The DFT method provides accurate vibrational data with standard deviations of less than $11\,cm^{-1}$, which correspond to groups not participating in significant intra- or inter-molecular interactions. A modification of the results using the empirical scaling factor 0.9614 was performed to achieve better correspondence between the experimental and theoretical values.

2.2. *Synthesis*

The free ligands **1** and **2** were obtained by reaction scheme 2 [18]. The Pd(II) complexes were obtained using the following procedure: 10 mL water solution containing 0.2232 g (0.1521 mol) of **1** or **2** is added to 10 mL solution containing 0.0885 g $PdCl_2$ (Merck, Germany) and 0.05 mL concentrated HCl under continuous stirring at 60°C for 2 h. After 1 week, the yellow precipitate was filtered off and dried under air (found for



X = N, Y = C (**1**)
X = C, Y = N (**2**)

Scheme 2. Reaction scheme for obtaining **1** and **2**.

Pd(II) complex with **1**: C, 54.01; H, 2.15; N, 4.48; found for Pd(II) complex with **2**: C, 53.90; H, 2.18; N, 4.47; [$C_{28}H_{18}N2O_4PdCl_2$] Calcd: C, 53.91; H, 2.19; N, 4.49%). The Pt(II) complexes with the same ligands were obtained as follows: 0.2232 g (0.321 mol) of the ligands are dissolved in 15 mL water and 15 mL aqueous solution of K_2PtCl_4 (0.2070 g, 0.022 mol) is added under continuous stirring and heating at 70°C for 15 h. After 1 month the obtained yellow precipitate was filtered off and dried in air. (Found for Pt(II) complex with **1**: C, 42.19; H, 2.55; N, 3.88; Found for Pt(II) complex with **2**: C, 47.18; H, 2.53; N, 3.91; [$C_{28}H_{18}N2O_4PtCl_2$] Calcd: C, 47.20; H, 2.55; N, 3.91%). The results from the used thermal methods show that in the temperature range 300–500K no solvent molecules are included in the complexes.

3. Results and discussion

3.1. *Conventional and linear-polarized IR-spectroscopic data*

The precise interpretation of the IR-spectroscopic data of the complexes requires detailed assignments of the IR-characteristic bands in the free ligands. Polarized IR-spectroscopy is a unique tool for experimental assignment of vibrations and structural and local structural information about oriented solids, analysis of **1** and **2** (scheme 1). Their nonpolarized IR and difference IR-spectra (Supplementary material) show a significant degree of macro-orientation of the suspended particles [15] leading to adequate assignment of IR-band to corresponding vibrational mode/s.

Comparison between these compounds with data of previously reported substituted esters shows within the 3100–3000 cm^{-1} IR-region a series of low-intensity bands corresponding to in-plane (i.p.) stretching vibrations (ν_{CH} and ν_{CH}^{Ar}) of both the coumarin and pyridine fragments. IR-bands of $\nu_{C=O}$ are observed at 1724 cm^{-1} in **1** and 1702 cm^{-1} in **2** (theoretical analysis 1726 cm^{-1} (**1**) and 1700 cm^{-1} (**2**)). These data are similar to those previously reported from different coumarins substituted by 3-phosphonic derivatives. The $\nu_{C=C}$ is observed at 1711 cm^{-1} (**1**) and 1677 cm^{-1} (**2**), respectively (theoretical value of $\nu_{C=C}$ 1710 and 1675 cm^{-1}). Looking at the differences between the theoretical and experimental values for each compound in **1**, a difference of 7 cm^{-1} is obtained, while in **2** the value is only 2 cm^{-1}. This is explained by a flat geometry of coumarin leading to conjugation between the C=C and C=O and shift of corresponding $\nu_{C=C}$. Within the range 1624–1500 cm^{-1} are observed a series of i.p. (a′) maxima of both the coumarin and the pyridine fragments. The corresponding out-of-plane (o.p.) bands are assigned **1**: 765 cm^{-1} (a″, coumarin fragment), 800 cm^{-1} (a″, pyridine); **2**: 759 cm^{-1} (a″, coumarin fragment), 801 cm^{-1} (a″, pyridine), respectively.

The a′ and a″ modes are assigned from C_s symmetry of the molecules. The first bands correlated well with other coumarin derivatives, where the IR-maximum is observed within 769–758 cm^{-1} [8–10]. Common for both **1** and **2** is the IR-band at 579 cm^{-1} corresponding to the o.p. mode ($\gamma_{C=O}$). The difference IR-LD spectrum of **1**, shown in Supplementary material, has an inflex point [19, 20] of the o.p. bands of both the aromatic fragments, indicating a near to co-planar disposition. These data correlated well with the theoretically predicted value of the dihedral angle of 2.1(2)°. The same result is obtained applying the reducing-difference procedure on the IR-spectroscopy patterns of **2**, where elimination of the bands at 759 and 801 cm^{-1} at equal dichroic ratio is observed. Similar to **1**, the results show a near planar geometry of **2**. Our theoretical calculations show that the dihedral angle between the plane of the coumarin and the pyridine fragments is 3.2(5)°, in accord with the experimentally proposed geometry.

The IR-spectra of the Pd(II) and Pt(II) complexes with **1** and **2** (Supplementary material) have the following main differences, compared to the ligands. For **1**, coordination with metal ions leads to a low frequency shift of the $\nu_{C=O}$ by 7 cm^{-1} in the Pd(II) and 6 cm^{-1} in corresponding Pt(II) complex; high frequency shift of about 8–10 cm^{-1} of the $\gamma_{C=O}$ bands is observed in both complexes. The i.p. and o.p. bands of the pyridine fragment in both complexes are observed at higher frequencies than those of the coumarin. Elimination of the o.p. bands of both the aromatic fragments leads to their simultaneous elimination at equal dichroic ratio, suggesting co-planar disposition of the structural fragments in the complexes. In the far IR-spectra of both complexes, two new IR-bands at 435 cm^{-1}/400 cm^{-1} (Pd(II) complex) and 457 cm^{-1}/398 cm^{-1} (Pt(II) complex) correspond to ν_{M-N} and ν_{M-O} stretching vibrations. In Pd(II) and Pt(II) complexes with **2**, only IR-bands from i.p. and o.p. of the pyridine are affected (7–11 cm^{-1}). In these complexes, o.p. a″ modes of the coumarin and pyridine fragments are eliminated at different dichroic ratios, indicating that coordination with the metal ions is accompanied by turning of the pyridine plane toward the coumarin plane. In the far IR of both complexes are observed new bands at 441 cm^{-1}/355 cm^{-1} in the Pd(II) complex of **2** and at 457 cm^{-1}/352 cm^{-1} in the Pt(II) complexes, assigned to ν_{M-N} and ν_{M-Cl} stretching vibrations [21]. The spectroscopic data show that **1** is bidentate with Pd(II) and Pt(II) through N_{py} and (C=)O, thus forming a stable six-membered chelate ring. Coordination leads to co-planarity of the pyridine and coumarin. In contrast, **2** is monodentate through N_{py}; each metal also has two Cl^- ligands. The steric interaction between these ions and the coumarin fragment can be the reason for turning the pyridine and coumarin planes and destroying planarity.

3.2. *Electronic spectra*

Comparing data of the free ligands, coordination of **1** and **2** leads to a bathochromic shift of the band about 240 nm (ε within 800–1010 $L\,mol^{-1}\,cm^{-1}$), corresponding to $n \rightarrow \pi^*$ transition of the C=O group in Pd(II) and Pt(II) complexes with **1**. In addition, a bathochromic shift of 15 nm for the $\pi \rightarrow \pi^*$ transition is also observed (ε within 12,300–13,070 $L\,mol^{-1}\,cm^{-1}$). Coordination of metal ions with **2** did not affect the $n \rightarrow p$ transition and a hypsochromic effect of 10 nm of the $\pi \rightarrow \pi^*$ transition is observed. These data are in accord with IR-spectra, due to distortion of the planar geometry of **2** during complexation, which causes a hypsochromic shift of the $\pi \rightarrow \pi^*$ transitions (Supplementary material).

3.3. *HPLC ESI MS/MS data*

The HPLC MS/MS of the ligands and corresponding metal complexes (Supplementary material) show highest *m*/*z* values of 554.18 ($t = 17.38$ min) corresponding to $[C_{28}H_{19}N_2O_4Pd]^+$ with a weight of 553.08, thus indicating the formation of the complex of **1** with Pd(II) at molar ratio 1 : 2. At the same experimental conditions, for the Pt(II) complex with **1,** a peak is observed at 798.51 *m*/*z* ($t = 20.13$ min) corresponding to the $4K^+$ adduct with $[C_{28}H_{19}N_2O_4Pt]^+$. The molar ratio of metal-to-ligand is also 1 : 2. The HPLC ESI MS/MS data for the compounds with **2** show a peak at *m*/*z* 624.21 for Pd(II) complex ($t = 15.52$ min), corresponding to $[C_{28}H_{19}N_2O_4PdCl_2]^+$ with a weight of 623.79. In the Pt(II) complex a peak at 871.57 ($t = 11.88$ min) belongs to the $4K^+$ adduct of $[C_{28}H_{19}N_2O_4PtCl_2]^+$. In the last two complexes the metal ions are coordinated with two ligand molecules and two Cl^-.

3.4. *^{1}H- and ^{13}C-NMR data*

Coordination of **1** and **2** with Pd(II) and Pt(II) only slightly affects chemical shifts in ^{1}H- and ^{13}C-NMR spectra of the ligand with typical signals about 8.50, 7.70 and 7.20 ppm observed. The corresponding ^{1}H- and ^{13}C-NMR data of **1** are 9.13 and 8.62 ppm (s, 1H), 8.77 ppm (d, $J = 7.11$ Hz), 7.82–7.66 ppm (m, 3H), 7.00 ppm (d, $J = 8.2$ Hz), 6.1 ppm (s, 1H); 188.3 (C=O), 148.66 (C-4), 131.3 (C-7), 129.6 (C-5), 124.23 (C-6), 121.22 (C-3), 113.44 (C-8). The corresponding data for **2** are 9.10 and 8.11 ppm (s, 1H), 8.61 ppm (d, $J = 6.7$ Hz), 7.71–7.61 ppm (m, 3H), 7.13 ppm (d, $J = 9.1$ Hz), 6.10 ppm (s, 1H); 188.2 (C=O), 147.9 (C-4), 131.6 (C-7), 129.1 (C-5), 124.2 (C-6), 121.3 (C-3) and 114.1 (C-8). A downfield shift of the pyridine signals in all of the complexes (7.70–8.10 ppm) of about 0.5–1.0 ppm is observed, indicating participation of the N_{py} in coordination (figure 1). The ^{13}C-NMR spectra at 155.00, 150.00, 135.00, 130.00, 125.00, 120.00 and 115.00 ppm are similar to previously reported ones of the free ligand and other derivatives [18, 22]. The C=O carbon shifts downfield, observed at 154.00 ppm (Pd(II) complex with **1**) and 150 ppm (Pt(II) complex with **1**). This confirms coordination of Pd(II) and Pt(II) with **1** through oxygen of C=O and N_{py}, while for coordination with **2** only N_{py} is coordinated.

4. Conclusions

Coordination between Pd(II) and Pt(II) and two 3-pyridinyl-coumarins are elucidated both in solution and solid-state by conventional and linear-polarized IR-spectroscopy of oriented colloid suspensions in nematic liquid crystal, ^{1}H- and ^{13}C-NMR, UV-Vis spectroscopy, positive, and negative mass spectrometry (ESI) as well as HPLC tandem mass spectrometry (HPLC-ESI-MS/MS), TGV, and DSC methods. The data for free ligands as well as quantum chemical DFT calculations of the electronic structure and vibrational properties support the experimental results. The following conclusions can

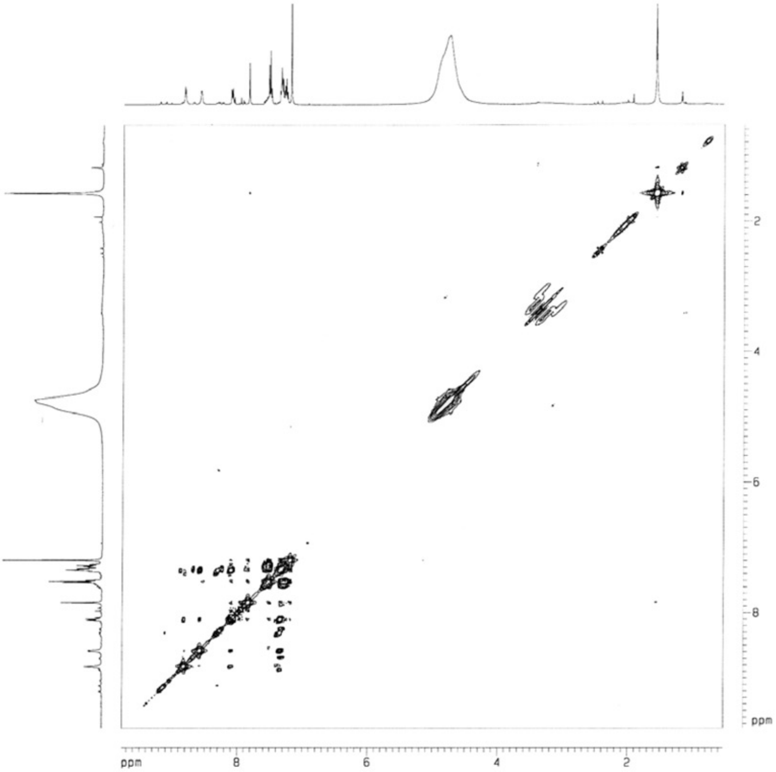


Figure 1. $^1H,^1H$-COSY spectrum of the Pt(II) complex with **2**.

be drawn: (i) coordination of Pd(II) and Pt(II) leads to formation of the mononuclear complexes with both ligands at a molar ratio of metal-to-ligand 1 : 2; (ii) suitable disposition of the O- and N_{py}-atoms in the first ligand leads to the formation of a stable six-member chelate ring and bidentate coordination of the ligand, while interaction of the Pd(II) and Pt(II) with the second ligand is monodentate. Chlorides complete the coordination; (iii) in HPLC-ESI-MS/MS data, the Pt(II) complexes correspond to the $4K^+$ adduct, while Pd(II) coordination compounds have only singly charged cations of each of the complexes.

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