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Cyclometallated Pt^{II} complexes of 2-(2-thienyl)-4-(cycloalkylimino)-substituted quinazolines

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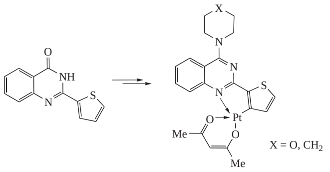
The title complexes were prepared based on 2-(thiophen-2-yl)-4-(morpholin-4-yl)- and 2-(thiophen-2-yl)-4-(piperidin-1-yl)-substituted quinazolines and found to exhibit luminescent properties.

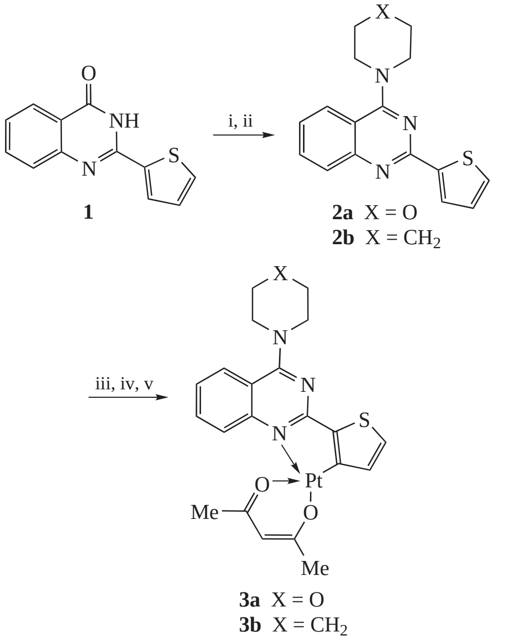


Nitrogen-containing six-membered heteroaromatic compounds, pyridines, quinolines, quinazolines and their aza and benzo analogues, are of interest as ligands to obtain organometallic complexes, photo- and electroluminescent compounds and various organic materials. Indeed, many π-deficient aza-aromatic systems based on azines and benzazines, including pyridines, pyrimidines, quinolines and quinoxalines, have already been used as key components for the formation of electron transport layers in electroluminescent materials.[1]

Cyclometallated platinum(II) complexes of aza-aromatic compounds have gained attention due to their high stability and intense emission.[2] Platinum(II) complexes with pyridine derivatives have been intensively studied since these organometallic materials demonstrate high quantum yields and large Stokes shifts. It is known that, in these complexes, a ligand not only provides strong binding with a metal, but it is also supposed to be a sensitizer, facilitating energy transfer to the metal center.[3] In particular, 2-(2-thienyl)pyridines (thpy) undergo cyclometallation, and the thpy complexes of Pt^{II} proved to exhibit enhanced lifetimes.[4] Aryl substituents were incorporated at the 5-position of the pyridine ring in order to expand the aromatic system,[5] and the same effect can be achieved by benzene ring annelation. Note that the Pt complexes of benzazines provide a good basis to develop electronic devices, which are capable of working in both visible and near-IR spectral regions.[6] The data on cyclometallated platinum complexes based on ligands from the benzazine family are scarcely available,[7] while the cyclometallated platinum(II) complexes of quinazolines have never been reported.

4-Morpholino- and 4-piperidino-2-(thiophen-2-yl)-substituted quinazolines **2a** and **2b**, respectively, have not so far been described, whereas a 6-methoxy analogue of **2a** has been mentioned.[8] 2-(Thiophen-2-yl)-4-piperazinoquinazoline, which is a close analogue of **2a** and **2b**, has been obtained previously through nucleophilic substitution of the chlorine atom at the 4-position of 2,4-dichloroquinazoline followed by a cross-coupling reaction with 2-thienylboronic acid.[9] It has also been shown that 4-morpholinoquinazoline can be obtained by oxidative alkylamination;[10] however, an electron-donating thienyl substituent at the 2-position of quinazoline deactivates the bicyclic system, thus making it reluctant toward direct amination. Quinazolines **2a** and **2b** were synthesized by the conversion of 2-(thiophen-2-yl)quinazolin-4-one **1** into a 4-chloro derivative followed by substitution of the chlorine atom under the action of cycloalkylimines (Scheme 1).

Ligands **2a** and **2b** were cyclometallated on reflux in acetic acid containing potassium tetrachloroplatinate according to a typical procedure,[11] resulting in the formation of dimeric complexes



Scheme 1 *Reagents and conditions*: i, POCl$_3$, reflux, 2 h, then NaHCO$_3$, H$_2$O; ii, morpholine or piperidine, MeCN, reflux, 10 h; iii, K$_2$PtCl$_4$, AcOH, reflux, 10 h; iv, DMSO, reflux, 5 min; v, sodium acetylacetonate, acetone, reflux, 16 h.

$[PtL(\mu\text{-}Cl)]_2$. The latter were treated with DMSO to afford the intermediate monomeric complexes PtL(DMSO)Cl, which were converted directly (without purification) into complexes **3a** and **3b** on treatment with an excess of sodium acetylacetonate in acetone (Scheme 1).

The structures of **2a**,**b** and **3a**,**b** were studied by ^{1}H NMR spectroscopy and mass spectrometry. The formation of complexes **3a**,**b** resulted in the disappearance of a one-proton signal of the thiophene ring and caused downfield shifts for the H(8) resonance signal of the quinazoline system. Moreover, the characteristic resonances of the acetylacetonate CH proton at 5.57–5.58 ppm and the signals of two methyl groups were observed in the ^{1}H NMR spectra. Molecular ion peaks in the mass spectra of complexes **3a**,**b** were recorded. An excellent correlation between experimental and calculated picks in the mass spectra of **3a**,**b** has been found (see Figures S6 and S8, Online Supplementary Materials).

According to the XRD data,[†] compound **3a** is crystallized in the centrosymmetric space group. The Pt ion has a typical distorted squared coordination. Bond lengths in the Pt chelate indicate at a strong conjugation in the 1,3-dicarbonyl system. As a result of the CH···O contact between C(9) an O(1) atoms (Figure 1), the benzene ring of the quinazoline system is turned toward the Pt(1)O(1)O(2)N(1)C(12) plane at an angle of 21°. In crystals, two molecules proved to form dimers on the twofold axes with the interatomic distance Pt···Pt [$1-x$, y, $0.5-z$] of 3.57 Å (Figure 2), which suggests the presence of Pt–Pt interaction in the crystal state.

Pt^{II} complexes **3** exhibit the long-wave shift of emission maximum compared to the starting ligands **2** (Table 1). Upon photoexcitation at the lowest energy band, the complexes and ligands were found to exhibit low-intensity luminescence with a large Stokes shift. The maxima in photoluminescence spectra of the complexes are red-shifted with respect to those observed for the ligand precursors.

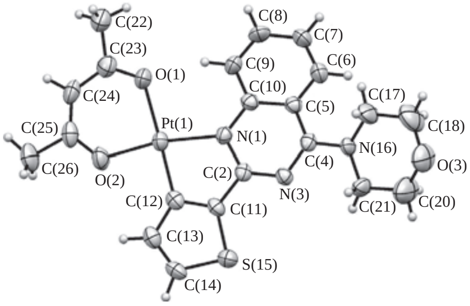


Figure 1 Molecular structure of **3a** in the thermal ellipsoids of 50% probability.

Table 1 Spectroscopic data of ligands **2** and complexes **3** in acetonitrile.

Compound	λ_{abs}/nm	λ_{em}/nm^a	Stokes shift/nm
2a	295, 335	502	167
2b	296, 335	508	173
3a	314, 355, 380	584	204
3b	314, 354, 377	579	202

^{a} Excitation at 335 nm for **2a**,**b** and at 380 nm for **3a**,**b**.

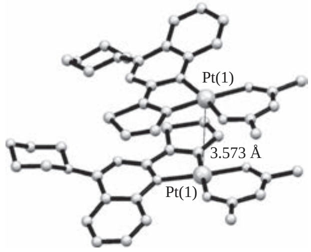


Figure 2 Dimer **3a** formation in a crystal.

In conclusion, the cyclometallated platinum(II) complexes [Pt(L)(acac)] with quinazolines have been prepared, and the spectroscopic data of quinazoline ligands **2** and their Pt complexes **3** have been compared. Further studies for the synthesis of new luminescent materials based on ligands **2** are in progress.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.03.015.

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[†] *Crystal data for* **3a**. The single crystal (red prism, 0.13×0.09×0.04 mm) of compound **3a** ($C_{21}H_{21}N_3O_3PtS$) was used for X-ray analysis. Analysis was performed at 295(2) K on an Xcalibur E diffractometer using graphite monochromated MoKα radiation (λ = 71.073 pm) and a CCD detector. An empirical absorption correction was applied (μ = 7.086 mm^{-1}). Crystal is orthorhombic, space group *Pbcn* with a = 17.3907(5), b = 15.1103(4) and c = 15.3554(5) Å, V = 4035.1(2) Å^3, Z = 8. On the angles $2.34 < \theta < 30.74°$ 14909 reflections were measured, among them 5654 unique reflections (R_{int} = 0.0518), 3282 reflections with $I > 2\sigma(I)$. Completeness to θ = 26.00° is 99.95%. The structure was solved by a direct method and refined by full-matrix least squares at F^2 using the SHELXTL program package.[12] All non-hydrogen atoms were refined anisotropically; the positions of the hydrogen atoms were calculated as a riding model in isotropic approximation. Goodness to fit at F^2 1.007; final R values [$I > 2\sigma(I)$], R_1 = 0.0422, wR_2 = 0.0623; R value (all reflections) R_1 = 0.0990, wR_2 = 0.0742. Largest difference peak and hole were 1.020 and –0.616 eÅ^{-3}.

CCDC 1439844 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.