Monatshefte für Chemie 131, 181–185 (2000)

**Monatshefte für Chemie**
**Chemical Monthly**

Printed in Austria

# Synthesis and Characterization of a New 2,2′-Azoquinoxaline and its Complexes with Platinum and Palladium

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**Summary.** Platinum and palladium dichlorides react readily with 2,2′-azoquinoxaline to give the di-$\mu$-chloro-2,2′-azo*bis*-(7,7′-*bis*-benzoyl-quinoxaline) diplatinum(II) and dipalladium(II) complexes. These crystalline complexes exhibit both metal-carbon binding and coordinate metal-nitrogene binding to azoquinoxaline.

**Keywords.** Oxime; Quinoxaline; Azoquinoxaline; Cyclometallation.

## Introduction

The chemistry of cyclometallated complexes is one of the most advanced area of modern organometallic chemistry [1–3]. These compounds are used in organic synthesis [4], catalysis [5–7], and asymmetric synthesis [8]. The cyclometallation reaction with Pt(II) and Pd(II) chlorides has been described more than 30 years ago [9], demonstrating that azo-benzene reacts with platinum(II) and palladium(II) chlorides to give complexes with carbon-to-metal $\sigma$-bonds. This fact has prompted us to search for similar reactions with 2,2′-azoquinoxaline compounds.

Over the last decade, we have synthesized novel phthalocyanines [10, 11] and oximes [12, 13] substituted with macrocyclic groups which have been shown to be capable of binding alkali and transition metal ions to form homo- and heteronuclear complexes. A route for the direct one-step synthesis of quinoxalin-2(1*H*)-one oxime has been reported which can be readily obtained by the reaction of aromatic *ortho*-diamines and *s-trans*-chloroethanedial dioxime and subsequent conversion to 2,2′-azoquinoxalines by the template effect of cobalt and nickel ions [14, 15]. This method is also applicable to 15-crown-5-quinoxalinone oxime derivatives to give the corresponding azo-quinoxalines which are soluble in common organic solvents, *e.g.* chloroform, dichloromethane, acetone *etc.* [16]. With tetraaminodibenzo-18-crown-6 as the starting material, an azoquinoxaline polymer contaning 18-crown-6 bridges has been synthesized [17].

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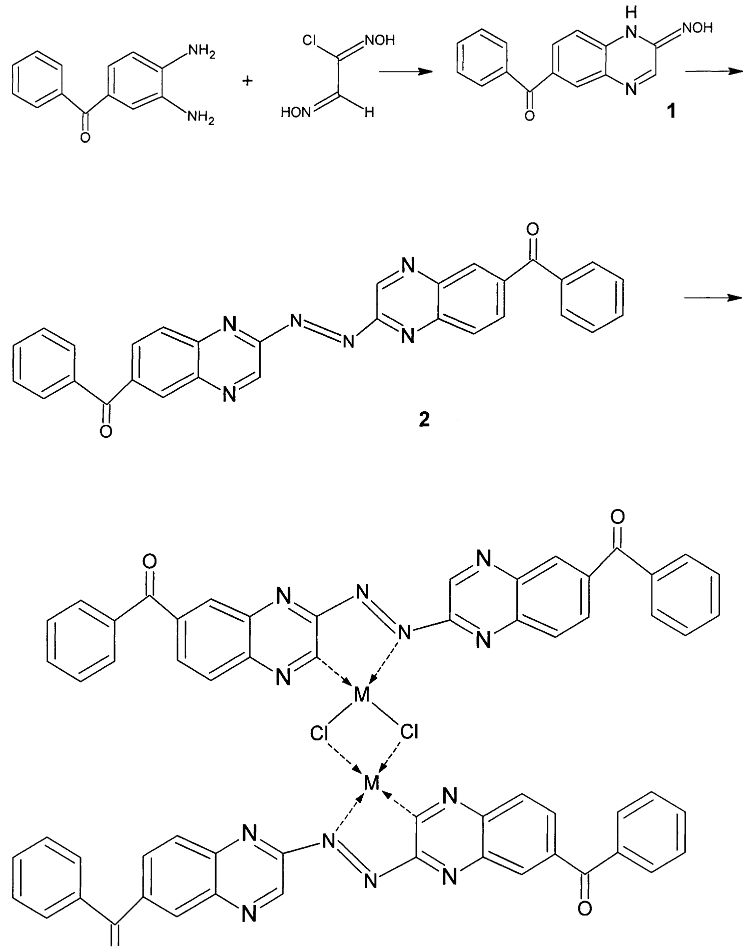
Here we describe the synthesis of a new 2,2′-azoquinoxaline and dinuclear cycloplatinated and -palladated azoquinoxalines complexes starting from 3,4-diaminobenzophenone and *s-trans*-chloroethanedial dioxime.

## Results and Discussion

In this work we describe a general route for the synthesis of the new 2,2′-azoquinoxaline **2** and its symmetrical dinuclear cyclometallated azoquinoxalines **3** and **4** ($M = Pt^{+2}$, $Pd^{+2}$) using the above mentioned starting materials (Scheme 1). 7-Benzoyl-quinoxalin-2(1*H*)-one oxime **1** was obtained by cyclization of 3,4-diaminobenzophenone with *s*-chloroethanedial dioxime without the addition of base. The reaction was carried out under a nitrogen atmosphere in order to avoid oxidation of the 3,4-diaminobenzophenone. The yield of this cyclization reaction between two bifunctional reagents was rather high (*ca.* 73%). The satisfactory elemental analysis results and the EI mass spectrum of **1** which shows the



**3**: $M = Pt^{+2}$

**4**: $M = Pd^{+2}$

**Scheme 1**

molecular ion peak at $m/z = 265$ (63%) confirmed the proposed structure. In the IR spectrum of **1**, NH and C=O absorptions were observed at 3320 and 1676 $cm^{-1}$. The characteristic bands for the oxime group were readily recognized at 3220 ($\nu_{OH}$), 1625 ($\nu_{C=N}$), and 990 $cm^{-1}$ ($\nu_{N–O}$). The $^1$H NMR spectrum of **1** shows two $D_2O$-exchangeable protons at 10.54 and 10.28 ppm for the OH and NH groups together with a singlet at 7.92 ppm for the azomethine group. In addition, the chemical shifts of the aromatic protons are observed as a multiplet at 7.76-7.25 ppm.

The condensation of the quinoxalin-2-one oxime to 2,2′-azoquinoxaline **2** was accomplished by the template effect of $CoCl_2$. The color of the solution gradually turned to dark red, and a bright crystalline organic compound precipitated. Comparison of the IR spectra of **2** and **1** confirmed the reaction by the disapperance of the NH and OH bands at 3320 and 3220 $cm^{-1}$. Bands due to C=O and C=N groups appeared at 1675 and 1610 $cm^{-1}$. The chemical shifts in the $^1$H NMR spectrum of **2** were found to be in agreement with the values reported for similar compunds [14–16]. The signal of the azomethine protons appeared as a singlet at 9.62 ppm. The multiplet at 8.59-7.93 ppm is due to aromatic protons. In contrast to the 2,2′-azobis-((15-crown-5)-eno[*g*]quinoxaline), **2** is only slightly soluble in *DMSO* and *DMF* [16]. This low solubility of **2** hindered an extensive $^{13}$C NMR investigation. Elemental analysis results closely followed the calculated values as expected. The EI mass spectrum of **2** showed a relatively intense $[M+2]^+$ (36%) peak instead of the $M^+$ peak. This behavior has been described to be characteristic for 2,2′-azoquinoxaline compounds [16].

Compound **2** was found to react readily with platinum(II) and palladium(II) chlorides to give dark blue products whose elemental analyses suggested that the di-$\mu$-chloro-2,2′-azo*bis*-(7,7′-*bis*-benzoyl-quinoxaline) diplatinum(II) (**3**) and dipalladium(II) (**4**) complexes were formed. The formation of the cyclometallated complexes was monitored in an experiment run with equimolar amounts of 2,2′-azoquinoxaline and platinum or palladium dichlorides in hot *DMF*. The dark blue crystalline products were obtained in good yields. The structures of complexes **3** and **4** are similar to the type found by *Cope* and *Siekman* for azobenzene [9]. Both complexes are stable to heat and storage. A common feature of these complexes is their limited solubility in organic solvents (slightly soluble in *DMSO* and *DMF*). Owing to their low solubility, no satisfactory NMR spectra could be obtained. The aromatic protons of **3** and **4** appeared as broad peaks at 7.58 and 7.57 ppm.

In summary, we can conclude that the reactions of platinum(II) and palladium(II) chlorides with azobenzenes discovered by *Cope* and *Siekman* are not limited to this system. In fact, they can be easily applied to 2,2′-azoquinoxaline compounds. It can be expected that cycloplatinated and -palladated 2,2′-azoqunoxaline complexes have application fields similar to their azobenzene analogues.

## Experimental

3,4-Diaminobenzophenone was purchased from Fluka. *s-trans*-Chloroethanedial dioxime was prepared by a reported procedure [18]. FTIR spectra were measured on an ATI Unicam Mattson 1000 spectrophotometer using KBr pellets. $^1$H NMR spectra were recorded on a Bruker 250 MHz spectrometer. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TÜBITAK Gebze Research Center; the results agreed satisfactorily with the calculated values (C, H, N, metal). Mass spectra were measured with a VG Zabspec GS-MS spectrometer. The metal content of the complexes was determined on a Zeeman 3030 Atomic Absorption spectrophotometer.

### *7-Benzoyl-quinoxaline-2(1H)-one oxime* (**1**; $C_{15}H_{11}N_3O_2$)

A solution of 2.12 g 3,4-diaminobenzophenone (10 mmol) in 100 $cm^3$ abs. ethanol was slowly added with stirring to a solution of 1.225 g *s-trans*-chloroethanedial dioxime (10 mmol) in 30 $cm^3$ abs. ethanol at room temperature under an $N_2$ atmosphere. After 10 min a yellow product started to precipitate; the reaction was completed after 2 h. After filtration, the solid was washed with hot $H_2O$ and then with cold ethanol and diethyl ether to give a bright yellow solid.

Yield: 1.93g (73%); m.p.: >210°C; $^1$H NMR (*DMSO*-$d_6$, $\delta$, 250 MHz): 10.54 (s, 1H, OH), 10.28 (s, 1H, NH), 7.92 (s, 1H, CH=N), 7.76-7.25 (m, 8H, Ar-H) ppm; IR (KBr): $\bar{\nu}$ = 3320 ($\nu_{(N-H)}$), 3220 ($\nu_{(O-H)}$), 3040 ($\nu_{(CH-Aro)}$), 1676 ($\nu_{(C=O)}$), 1625 ($\nu_{(C=N)}$), 990 ($\nu_{(N-O)}$) $cm^{-1}$; MS (EI): *m/z* = 265 (63%, $M^+$); UV/Vis (*DMSO*): $\lambda_{max}$ ($\varepsilon$) = 427 (4890) nm.

### *2,2′-Azobis-(7,7′-bis-benzoyl-quinoxaline)* (**2**; $C_{30}H_{18}N_6O_2$)

To a solution of 0.265 g **1** (1 mmol) in 45 $cm^3$ abs. ethanol, a solution of 0.12 g $CoCl_2 \cdot 6H_2O$ (0.5 mmol) in 10 $cm^3$ abs. ethanol was added. The mixture was stirred at 60°C under a nitrogen atmosphere for 6 h. The color of the solution turned to dark red from the initial green color. A reddish-brown precipitate was obtained when the solution was cooled to room temperature. It was filtered, washed with hot ethanol and then diethyl ether, and dried *in vacuo*.

Yield: 0.15 g (65%); m.p: >220°C; $^1$H NMR (*DMSO*-$d_6$, $\delta$, 250 MHz): 9.62 (2H, N=CH), 8.59-7.93 (16H, Ar-H) ppm; IR (KBr): $\bar{\nu}$ = 3080 ($\nu_{(CH-Aro)}$), 1675 ($\nu_{(C=O)}$), 1610 ($\nu_{(C=N)}$) $cm^{-1}$. MS (EI): *m/z* = 496 (36%, $[M+2]^+$); UV/Vis (*DMSO*): $\lambda_{max}$ ($\varepsilon$) = 352 (18440), 501 (7100), 535 (7320), 577 (7250), 629 (6680) nm.

### *Di-μ-chloro-2,2′-azobis-(7,7′-bis-benzoyl-quinoxaline) diplatinum* (**3**; $C_{60}H_{34}Cl_2N_{12}O_4Pt_2$)

A heterogenous mixture of 0.100 g **2** (0.20 mmol) and 53 mg $PtCl_2$ (0.20 mmol) in 40 $cm^3$ *DMF* was stirred at 100°C. After 2 h, all of the $PtCl_2$ had dissolved and the color of the solution turned dark-blue. The mixture was cooled to room temperature, and water was added. The dark-blue precipitate was filterad off and washed with hot water, cold *DMF*, ethanol, and diethyl ether.

Yield: 0.100 g (40.95%). m.p.: >220°C; $^1$H NMR (*DMSO*-$d_6$, $\delta$, 250 MHz): 8.17 (s, 2H, N=CH), 7.58 (b, 32H, Ar–H) ppm; UV/Vis (*DMSO*): $\lambda_{max}$ ($\varepsilon$) = 455 (24600), 574 (2460) nm; IR (KBr): $\bar{\nu}$ = 3050 ($\nu_{(CH-Aro)}$), 1651 ($\nu_{(C=O)}$), 1610 ($\nu_{(C=N)}$) $cm^{-1}$.

### *Di-μ-chloro-2,2′-azobis-(7,7′-bis-benzoyl-quinoxaline)dipalladium* (**4**; $C_{60}H_{34}Cl_2N_{12}O_4Pt_2$)

This dark-blue complex was prepared following the same procedure as described for **3** starting from 0.100 g **2** (0.20 mmol) and 35 mg $PdCl_2$ (0.20 mmol).

Yield: 0.110 g (43%); m.p.: >220°C; $^1$H NMR (*DMSO*-$d_6$, $\delta$, 250 MHz): 8.20 (s, 2H, CH=N), 7.57 (b, 32H, Ar–H) ppm; UV/Vis (*DMSO*): $\lambda_{max}(\varepsilon)$ = 578 (2560) nm; IR (KBr): $\bar{\nu}$ = 3050 ($\nu_{(CH-Aro)}$), 1650 ($\nu_{(C=O)}$), 1608 ($\nu_{(C=N)}$) $cm^{-1}$.

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*Received July 16, 1999. Accepted (revised) October 22, 1999*