Synthesis and Structures of Rh and Ru Metal Complexes of *o*-Benzoquinonediimine and Diiminosuccinonitrile*

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Transition metal complexes with delocalized ground states, *e.g.* the complexes of *o*-benzoquinonediimine and diiminosuccinonitrile, are of considerable interest owing to their unusual spectroscopic, magnetic, redox, and structural properties. A few Ru complexes of *o*-benzoquinonediimine have been reported [1–3], but only $[Ru(bqdi)(bipy)_2](PF_6)_2$ has been structurally characterized [3]. Here we report the synthesis and Rh and Ru metal complexes of *o*-benzoquinonediimine and diiminosuccinonitrile, and the structural analysis of $[Rh^{II}(PPh_3)_2Cl(s\text{-}bqdi)]$ and $[Ru^{II}(disn)Cl_2(CH_3CN)_2]$. Reaction of the Wilkinson's catalyst, $RhCl(PPh_3)_3$, with *o*-phenylenediamine or diaminomaleonitrile in the presence of air in CH_3CN leads to a rapid formation of a crystalline, air-stable green solid **1**. The metal-assisted ligand oxidations [4, 5] occur after the ligand substitutions as follows:

$$[Rh^{I}Cl(PPh_3)_3] \xrightarrow{L} [Rh^{I}Cl(PPh_3)_2L] \xrightarrow{O_2} \underset{\mathbf{1}}{[Rh^{II}Cl(PPh_3)L']}$$

L = opda or damn; L′ = s-bqdi or s-disn.

Complexes (1) show the following pertinent spectroscopic data: $[Rh^{II}Cl(PPh_3)_2(s\text{-}bqdi)]$ ν_{N-H} at 3335, 3290, 3260 cm^{-1}; $[Rh^{II}Cl(PPh_3)_2(s\text{-}disn)]$ ν_{N-H} at 3340, 3325, 3230 cm^{-1} and $\nu_{C\equiv N}$ at 2205 cm^{-1}, visible absorptions at 650 nm (5.17×10^3), 500 nm (2.01×10^3) and 390 nm (3.69×10^3).

The crystal structure of $[Rh^{II}(PPh_3)_2Cl(s\text{-}bqdi)]$ is shown in Fig. 1. The Rh atom is bound to two phosphorus atoms of triphenylphosphine, one chlorine atom, and two nitrogen atoms of semi-*o*-benzoquinonediimine, and has a coordination geometry between a square pyramid (P2 as apex) and a trigonal bipyramid (Cl and N2 as apices). The main interest with this structure is the bonding of the semi-*o*-benzoquinonediimine ligand. The lengths of the C–N bonds (av. 1.351 Å) and their conjugated C–C bonds (av. 1.367 Å) are very close to those in $[Ni^{II}(s\text{-}bqdi)_2]$ [6], $[Co^{II}(s\text{-}bqdi)_2]$ [7] and $[Co^{III}Cl(s\text{-}bqdi)_2]$ [7] which have pronounced delocalized electronic structures, but longer than in $[Fe^{II}(bqdi)_3]^{2+}$ [7] which has a localized double bond arrangement (C–N, 1300 Å; C–C, 1.339 Å). Very few monomeric Rh^{II} complexes have been characterized.

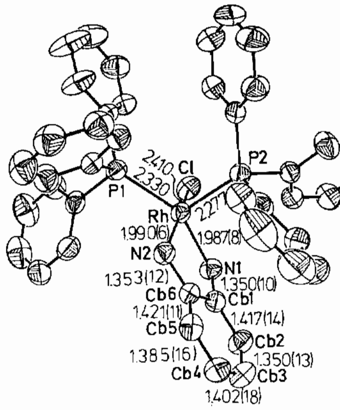

Fig. 1. ORTEP Drawing of $[Rh^{II}Cl(PPh_3)_2Cl(s\text{-}bqdi)]$ in the crystal. Space group $P2_1/c$, $a = 13.608(3)$, $b = 18.704(6)$, $c = 18.238(6)$ Å, $\beta = 115.23(2)°$, $Z = 4$; 3380 reflections with $F > 3\sigma(F)$, 433 parameters, $R = 4.3\%$, $R_w = 4.4\%$.

The reaction of $RuCl_3 \cdot (H_2O)_x$ with diaminomaleonitrile or *o*-phenylenediamine in CH_3CN leads to the formation of a wine-red solution. Red crystals were obtained after adding water to the solution. The complex $[RuCl_2(CH_3CN)_2(disn)] \cdot (H_2O)$ has the following spectroscopic data: IR at 3385 (ν_{O-H}), 3140, and 3160 (ν_{N-H}), 2240 and 2233 cm^{-1} ($\nu_{C\equiv N}$) visible absorptions at 517 nm (6.56×10^3), 360 nm (6.59×10^3) and 315 nm (6.81×10^3).

The results of the X-ray structural analysis for the complex $[Ru^{II}Cl_2(disn)(CH_3CN)_2]$ are shown in Fig. 2. The Ru atom has a slightly distorted octahedral coordination. The 'bite' of the diiminosuccinonitrile is such that the N–Ru–N angle is compressed from 90° to 79°. This distortion results in the remaining ligand–Ru–ligand angles deviating from 90°. The very short Ru–N distances (1.968 Å) indicate strong bonding between the Ru^{II} and the diiminosuccinonitrile ligand. The bonding in the diiminosuccinonitrile ligand is of particular interest. The two imine C–N bonds (av. 1.304 Å) are short, consistent with their identification as localized double bonds. The bond length of C1–C2 (1.433 Å) is only slightly shorter than the value of a C–C single bond in cyclo-

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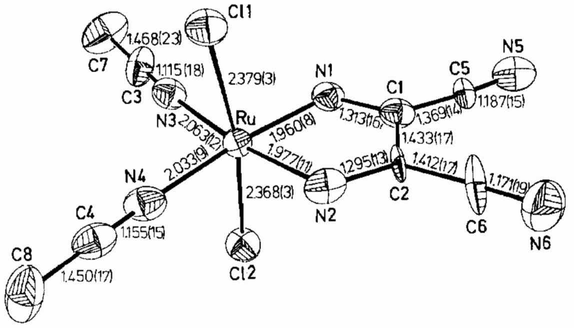

Fig. 2. ORTEP Drawing of [$Ru^{II}Cl_2(CH_3CN)_2$(disn)] in the crystal. Space group $P2_1/a$, $a = 13.709(11)$, $b = 9.819(5)$, $c = 10.980(8)$ Å, $\beta = 105.32°$, $Z = 4$; 1943 reflections with $F > 6\sigma(F)$, 163 parameters, $R = 7.7\%$, $R_w = 6.5\%$. The crystals might be multiple; ω scan was used for data collection, and a high cut-off for unobserved reflections was applied.

octatetraene (1.46 Å). The ligand has a more localized electronic state than in other complexes of semi- (or anionic) diiminosuccinonitrile, *e.g.* [Ni^{II}(s-disn)$_2$] [8], [Co^{III}(CN)(s-disn)$_2$] [9], [Co^{I}(s-disn)$_2$]$^-$ [10]. This is the first structural report on a neutral diiminosuccinonitrile complex.

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