Unique Eclipsed Cofacial Oligomeric Complexes of Rhodium containing Three-layered Bonding of 9,10-Phenanthroquinonediimine

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The synthesis and crystal structures of three unique metal complexes containing synergic multi-layered metal–metal bonds and ligand–ligand bonds are described.

π–π Interactions between highly conjugated molecules, *e.g.* TTF–TCNQ complex, play important roles in electron transport processes.[1] d_{z^2} Interactions in partially oxidized d^8 square planar complexes contribute to their properties of anisotropic electrical conductivity.[1] We have reported a few examples of dimeric bonding interactions of metal complexes that contain synergic metal–metal bonds and ligand–ligand bonds.[2–5] Here, we report three novel structures of metal complexes of 9,10-phenanthroquinonediimine and 9,10-phenanthrosemiquinonediimine ligands that exhibit synergic multi-layered metal–metal bonds and ligand–ligand bonds.

The dark-green binuclear complexes $[Rh^I(s\text{-}pqdi)(CO)_2]_2$, **5** were synthesized by the reaction of phda, 9,10-diaminophenanthrene, **1**, with $[RhCl(CO)_2]_2$, **4**, in MeCN followed by oxidation by air (Scheme 1).†

The crystal structure of **5** consists of discrete acetonitrile-solvated dimeric complexes, $[Rh^I(s\text{-}pqdi)(CO)_2]_2{\cdot}MeCN$ (s-pqdi = 9,10-phenanthrosemiquinonediimine).‡ A similar structure has been observed in $[Rh^I(s\text{-}disn)(CO)_2]_2$.[5] (s-disn = semi-diiminosuccinonitrile). It was proposed that there is one Rh^I–Rh^I bond and one δ-type bond between the pair of s-pqdi ligands.[4,5]

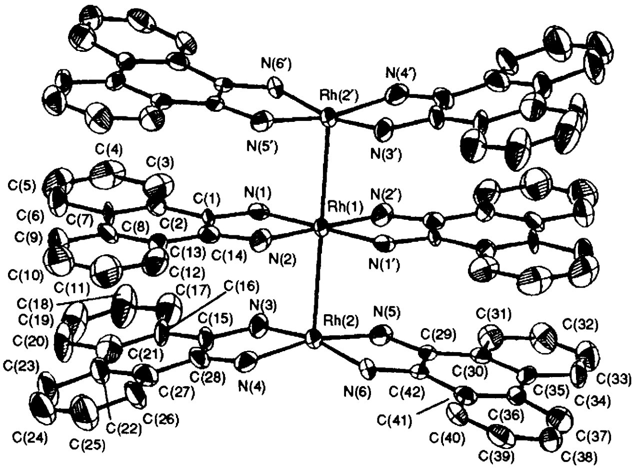


Fig. 1 ORTEP drawing of the $[Rh^I_4(s\text{-}pqdi)_2(pqdi)_4(CO)_4]^{2+}$, **6**

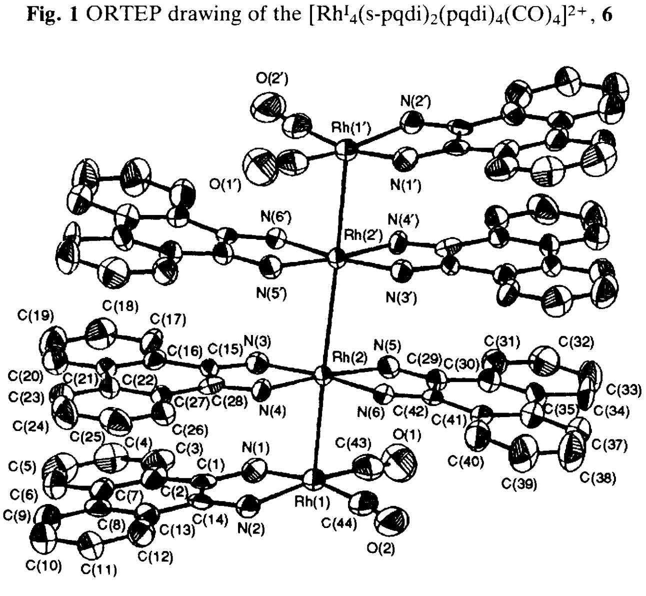
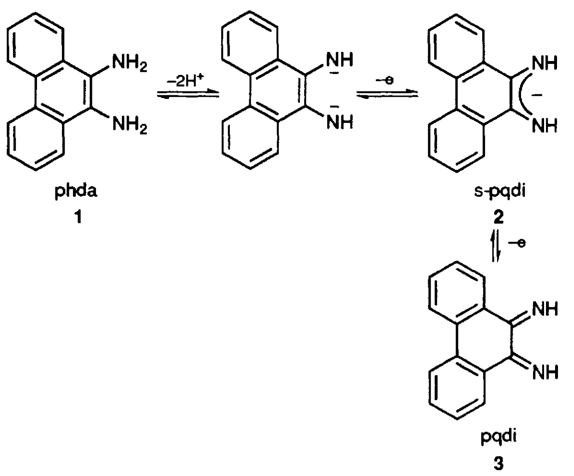
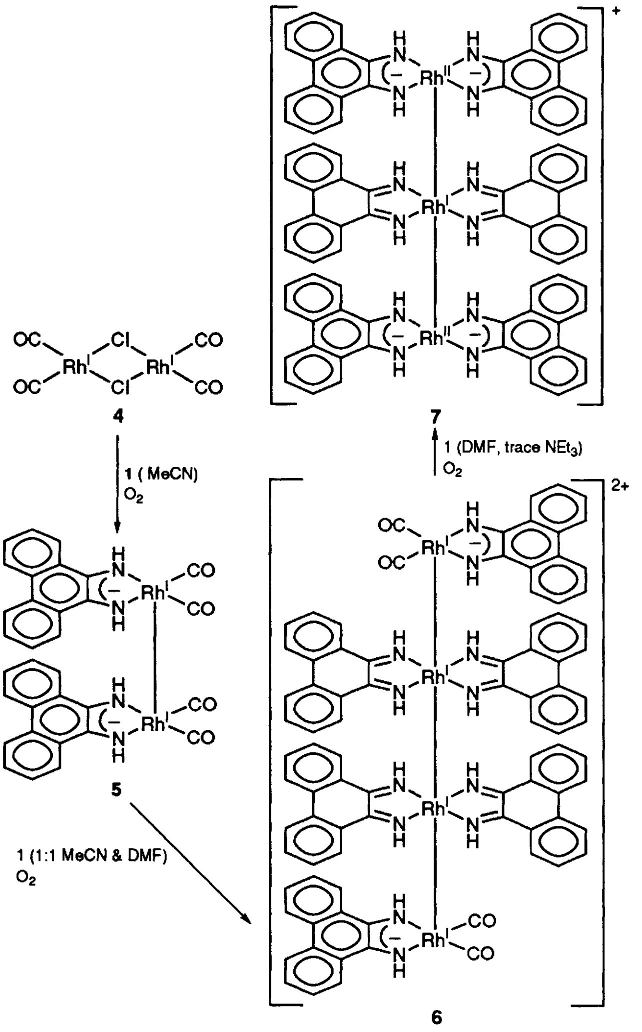


Fig. 2 ORTEP drawing of the $[Rh^{II}_2Rh^I(s\text{-}pqdi)_4(pqdi)_2]^+$, **7**

Following the substitution of CO of **5** by **1** in dmf, subsequent oxidation of the ligand and dimerization of the complexes led to formation of red–purple tetrametallic complexes **6**. The crystal structure of **6** consists of discrete cation $[Rh^I_4\ (s\text{-}pqdi)_2(pqdi)_4(CO)_4]^{2+}$ (pqdi = 9,10-phenanthroquinonediimine), anion Cl^- and dmf molecules (Fig. 1).§ The crystallographic centre of inversion is located between Rh(2) and Rh(2′) atoms of the cation. The unprecedented four-decker cation has a nearly linear tetranuclear metal chain with $Rh^I(1)$–$Rh^I(2)$, 2.848(1) Å, $Rh^I(2)$–$Rh^I(2')$, 2.858(1) Å, and Rh(1)–Rh(2)–Rh(2′), 160.2(4)°. The Rh(1) atom is displaced 0.194(5) Å from the plane formed by the four coordinating atoms (N_2C_2) toward the Rh(2) atom and the latter Rh(2) atom is displaced 0.070(4) Å from the plane formed by the four coordinating nitrogen atoms toward Rh(2′) atom. The d^8–d^8 metal–metal bonds are rather uncommon, although several have been characterized.[2,3,5,6] This is the first example of oligomeric d^8 Rh^I metal-chain system. Second, the three pqdi and s-pqdi ligands on each side are arranged in an eclipsed conformation. The central layer of pqdi ligands are slightly twisted [torsional angles: N(1)–Rh(1)–Rh(2)–N(3) 6.4(2), N(2)–Rh(1)–Rh(2)–N(4) 3.5(2), N(3)–Rh(2)–Rh(2′)–N(6′) −3.5(2), N(4)–Rh(2)–Rh(2′)–N(5′) −4.2(2)°] to minimize the repulsive forces of the six-membered rings. The five-membered chelate rings of three layers of ligands are separated by 3.0 Å. The facial approach of three such monomeric α-diimines leads to splitting of three parallel π-orbitals. Splitting of the antibonding orbitals and occupation of the lower orbital would lead to a net stabilization of eclipsed conformation. This bonding we name a three layered δ-type bond. Third, the bond pattern of the ligands coordinating to Rh(2) is typical of coordinating pqdi, **3**, with an average C–N length 1.30(1) and C–C length 1.46(1) Å in a five-membered chelate ring,[7,8] but the bond pattern of the ligand coordinating to Rh(1) is that of coordinated s-pqdi, **2**, with an average C–N length 1.33(1) and C–C length 1.42(1) Å.[5]





The further substitution of CO of **6** by **1** followed by oxidation of the ligand and cleavage of one terminal M–M bond led to formation of a red-purple trimetallic complex **7**. The crystal structure of **7** consists of discrete cation $[Rh^{II}_2Rh^I(s\text{-}pqdi)_4(pqdi)_2]^+$, anion Cl^- and solvated dmf molecules (Fig. 2).§ There are two crystallographically independent trimeric cations, both are centrosymmetric with the central Rh atom located at the special position $(\bar{1})$. The unique three-decker cation has a linear trinuclear metal chain with $Rh^{II}(2)$–$Rh^I(1)$, av. 2.754(2) Å, which is intermediate between that of a Rh^{II}–Rh^{II} bond, 2.624(1) Å in $[Rh_2(CH_3CN)_{10}]^{4+}$[9] and that of Rh^I–Rh^I, 2833(2) Å in $[Rh(s\text{-}disn)(CO)_2]_2$ (s-disn = semi-diiminosuccinonitrile),[5] 2.923(1) Å in **5** 2.853(2) Å in **6**. We propose that these metal–metal bonds are three-centred σ-bonds arising from the overlap of d_{z^2} orbitals. Second, all pqdi and s-pqdi ligands are arranged in an eclipsed conformation. Like **6**, the central layer of pqdi ligands is twisted [torsional angles: N(1)–Rh(1)–Rh(2)–N(3) 8.5(3), N(2)–Rh(1)–Rh(2)–N(4) 9.6(3), N(1)–Rh(1)–Rh(2′)–N(6′) −8.4(3), N(2)–Rh(1)–Rh(2′)–N(5′) −8.1(3)°] to minimize the repulsive forces of the six-membered rings. The twisted angle of **7** is larger than that of **6** because of the smaller interplanar distance of **7** (2.9 Å). The three-layered δ-type bond is believed to be the reasonable explanation for the eclipsed conformation. The bond pattern of the ligands coordinating to Rh(1) is an intermediate of coordinated **2** and **3** with an average C–N length 1.32(2) and C–C length 1.43(2) Å in the five-membered chelate ring, but the bond pattern of the ligands coordinate to Rh(2) is that of coordinated **3** with a C–N length 1.33(2) and 1.42(2) Å, the large error on bond parameters prevents any further detailed comparison.

The iridium analogues can also be prepared by starting from $[Ir(acac)(CO)_2]$.

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Footnotes

† *Spectral data* for complex **5**: diamagnetic, δ $[(CD_3)_2SO]$ 10.21(NH), 6.40–7.92 (aromatic CH); ν_{N-H}/cm^{-1} = 3355, 3317, $\nu_{C\equiv O}$ = 2057, 2037, 1993, 1967; λ_{max}/nm = 735 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$, 1.73×10^4), 463 (1.92×10^4), 397 (3.02×10^4).

Spectral data for complex **6**: diamagnetic, δ $[(CD_3)_2SO]$ 11.77, 11.03, 10.79 (NH), 6.40–8.60 (aromatic CH); ν_{N-H}/cm^{-1} = 3431, $\nu_{C\equiv O}$ = 2035, 1988; λ_{max}/nm = 445 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$, 1.61×10^4), 386 (1.90×10^4).

Spectral data for complex **7**: diamagnetic, δ $[(CD_3)_2SO]$ 12.41, 11.80 (NH), 7.18–8.41 (aromatic CH); ν_{N-H}/cm^{-1} = 3449; λ_{max}/nm = 521 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$, 1.81×10^4), 372 (2.91×10^4).

‡ *Crystal data*: $[Rh^I(s\text{-}pqdi)(CO)_2]_2 \cdot CH_3CN$, orthorhombic, space group $P2_12_12_1$, a = 11.832(7), b = 18.662(7), c = 27.506(7) Å, V = 6074(4) $Å^3$, D_m = 1.69(1), D_c = 1.687 g cm^{-3}, Z = 8; diffractometer (CAD4) with graphite-monochromated Mo-Kα radiation. ψ scan absorption correction was made (T_{min} & T_{max}, 0.89 & 1.00, respectively); 5894 unique reflections ($2\theta < 50°$) were measured and 5071 reflections with $I > 2\sigma(I)$ were used in the refinement. The refinement of the positional and anisotropic thermal parameters for all non-hydrogen atoms (812 variables) converged to R = 0.029 and R_w = 0.029.

§ *Crystal data* for $[Rh^I_4(s\text{-}pqdi)_2(pqdi)_4(CO)_4]Cl_2 \cdot (dmf)_7 \cdot (H_2O)_2$, monoclinic, space group $P2_1/c$, a = 13.540(2), b = 25.170(8), c = 16.533(7) Å, β = 111.93(3)°, V = 5227(3) $Å^3$, D_m = 1.46(1), D_c = 1.459 g cm^{-3}, Z = 2. The refinement of the positional and anisotropic thermal parameters for all non-hydrogen atoms (except one disordered dmf molecule which is refined isotropically) (641 variables and 3704 reflections) converged to R = 0.046 and R_w = 0.043. For $[Rh^{II}_2Rh^I(s\text{-}pqdi)_4(pqdi)_2]Cl \cdot (dmf)_3$, triclinic, space group $P\bar{1}$, a = 15.665(5), b = 16.181(7), c = 19.104(3) Å, α = 96.40(3), β = 107.04(3), r = 117.23(4)°, V = 3941(2) $Å^3$, D_m = 1.51(1), D_c = 1.518 g cm^{-3}, Z = 2; The refinement of the positional and anisotropic thermal parameters for all non-hydrogen atoms (1039 variables and 5609 reflections) converged to R = 0.068 and R_w = 0.066. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallograpic Data Centre. See Information for Authors, Issue No. 1.

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