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A Novel Chain Compound Composed of Rhodium(II) Pivalate Dimer and 1,4-Benzoquinone

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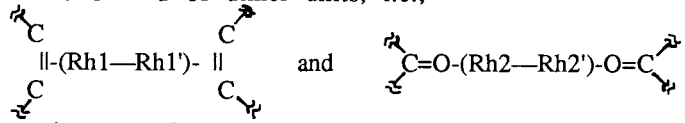
The reaction of rhodium(II) pivalate dimer, $Rh_2(O_2CCMe_3)_4$ with 1,4-benzoquinone (BQ) in hexane gave a chain complex, $[Rh_2(O_2CCMe_3)_4 \cdot BQ]_n$, where the rhodium(II) pivalate dimers are connected by the bifunctional ligation of the *p*-quinone through its carbonyl oxygen or C=C double bond.

Recently, many types of polymeric transition metal complexes bridged by the ligands have been presented.[1] In the previous paper, we introduced *p*-quinone as a bridging ligand for $Mo_2(O_2CCR)_4$ dimer.[2] The structural analysis of the isolated compound, $[Mo_2(O_2CCF_3)_4 \cdot AQ]_n$ (**1**) (AQ=9,10-anthraquinone), showed some degree of interaction between the dimer unit and bridging ligand. We consider this interaction is the first step for producing the low-dimensional properties. Our further interest is now devoted to the effect on the structural feature by the variation of the dimer unit in combination with the bridging ligand, *p*-quinone. Here, we report a chain complex $[Rh_2(O_2CCMe_3)_4 \cdot BQ]_n$ (BQ=1,4-benzoquinone) (**2**) prepared by the reaction of rhodium(II) pivalate ($Rh_2(O_2CCMe_3)_4$) and 1,4-benzoquinone in hexane.

The compound **2** was obtained as follows. A solution of 1,4-benzoquinone (10 mg, 0.09 mmol) in dry hexane (10 ml) was added to a solution of rhodium(II) pivalate (50 mg, 0.08 mmol) in dry hexane (10 ml) under argon. After stirring the solution for 5 h at room temperature, a precipitate was filtered, washed with hexane, and dried in vacuo. Anal. Found: C, 43.73; H, 5.56%. Calcd for $C_{26}H_{40}O_{10}Rh_2$: C, 43.47; H, 5.61%.

The X-ray crystal structure[3] of **2** is shown in Fig. 1. The chain structure is formed by alternated arrangement of $Rh_2(O_2CCMe_3)_4$ and 1,4-benzoquinone. However, the bonding feature between the dimer unit and *p*-quinone is different from that observed in **1**, where the quinone links through its both carbonyl oxygens. In the case of **2**, one carbonyl oxygen ligates to a dimer unit (the distance Rh2-O20 is 2.289(3) Å), but the other one (O10) does not participate in the coordination. Alternatively, a C=C double bond of the quinone is approached to an axial site of the neighbouring dimer unit. The distances of Rh-C, 2.439(4) (for Rh1-C5) and 2.488(5) Å (for Rh1-C6) are enough short for bonding. This type of bonding is rare, because only one example, an

axial bisolefin complex $Rh_2(O_2CCF_3)_4$((-)-*trans*-caryophyllen)$_2$ (**3**),[4] is known so far. In **3**, the Rh-C distances are 2.46(1), 2.62(1), and 2.63(1) Å. In addition, it should be noted that the chain structure of **2** consists of two kind of dimer units, i.e.,



In the 1,4-benzoquinone moiety, no considerable structural change is observed except for the elongation of axially coordinated C=C bond (C5-C6 1.346(7) Å) (the corresponding distance of free 1,4-benzoquinone is 1.322(8) Å[5]). The elongation of C=C bond has been observed in other π-complexes of *p*-quinones.[6] Relatively small elongation is observed in **2**. However, it is notable that the axial interaction of the C=C bond is stronger than that of the

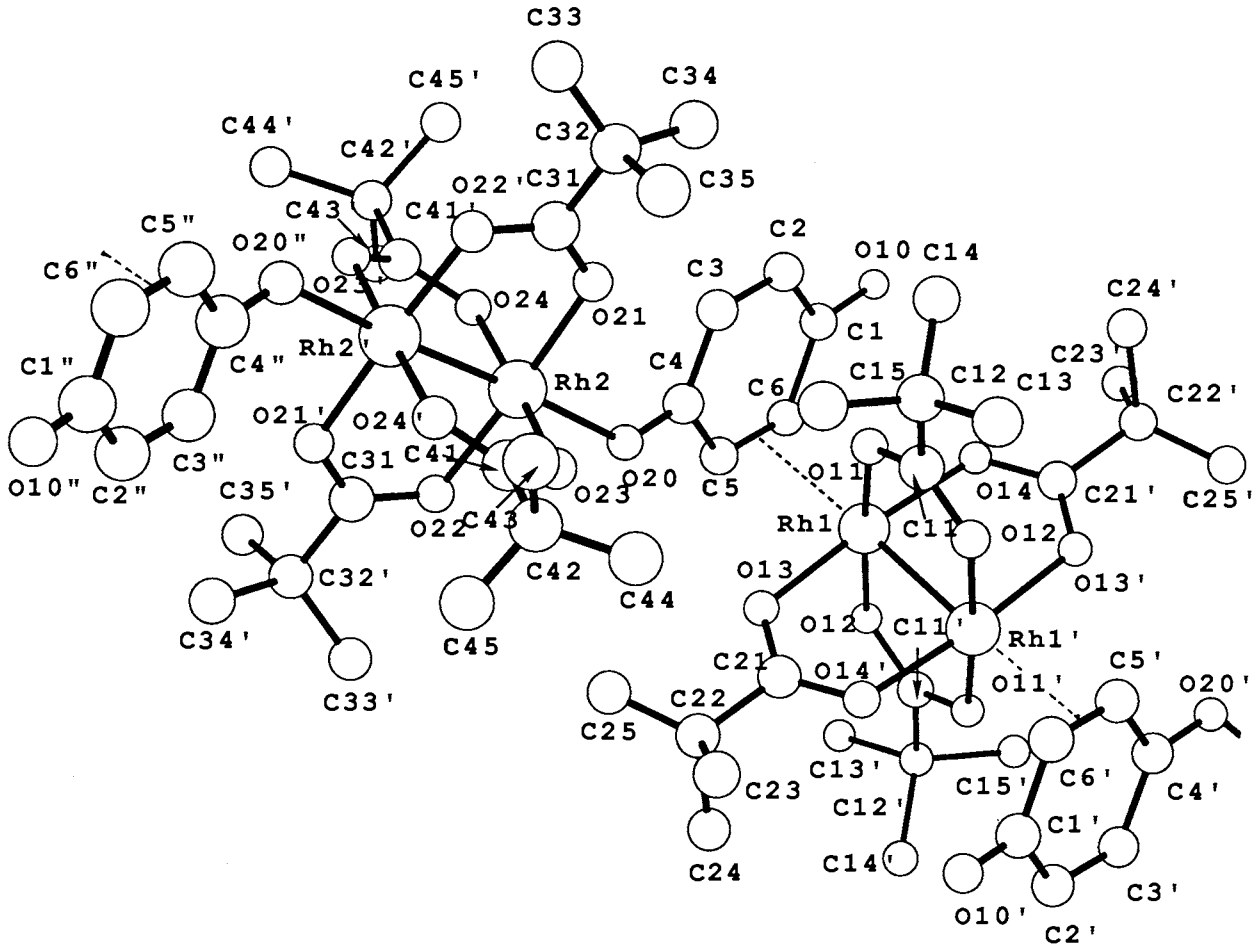


Fig. 1. Structure of a portion of a chain structure of $[Rh_2(O_2CCMe_3)_4 \cdot BQ]_n$ (**2**). Crystallographic inversion centers exist in the center of each Rh_2 dimer unit. Selected bond distances (*l*/Å) and angles (ϕ/°) are: Rh1-Rh1' 2.403(1), Rh1-O(pivalate) 2.023(average), Rh1-C5 2.439(4), Rh1-C6 2.488(5), Rh2-Rh2' 2.375(1), Rh2-O(pivalate) 2.031(average), Rh2-O20 2.289(3), C1-C2 1.471(7), C1-C6 1.474(9), C2-C3 1.324(8), C3-C4 1.454(8), C4-C5 1.488(6), C5-C6 1.346(7), C1-O10 1.218(8), C4-O20 1.223(6), Rh1'-Rh1-C5 162.1(1), Rh1'-Rh1-C6 166.0(1), Rh2-O20-C4 133.4(3), Rh2'-Rh2-O20 171.8(1).

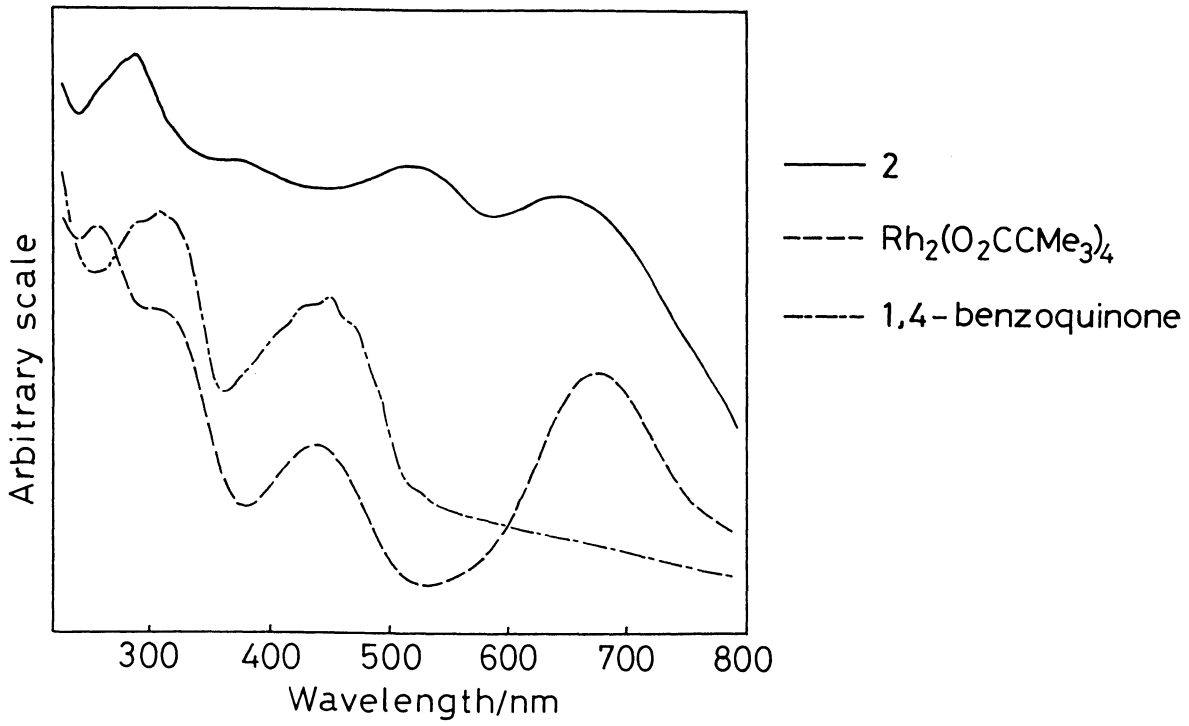


Fig. 2. Diffuse reflectance spectra of **2**, $Rh_2(O_2CCMe_3)_4$, and 1,4-benzoquinone.

carbonyl in **2**, the bond length of Rh1-Rh1' (2.403(1) Å) being longer than that of Rh2-Rh2' (2.375(1) Å).[4,7]

Diffuse reflectance spectrum of **2** is shown in Fig. 2, together with those of $Rh_2(O_2CCMe_3)_4$ and 1,4-benzoquinone. The band around 650 nm in **2** corresponds to that at 675 nm in $Rh_2(O_2CCMe_3)_4$ which is attributable to $\pi^*-\sigma^*$ transition in the Rh_2 core.[7] The $\pi^*-\sigma^*$ transition band is sensitive to the axial ligation[7] and the 675 nm band may be blue-shifted on the formation of the chain compound. The band around 510 nm in **2** may be tentatively assigned to the $\pi^*-\sigma^*$ (Rh-O) transition band,[7] which is observed at 440 nm in $Rh_2(O_2CCMe_3)_4$, because the band at ca. 450nm of 1,4-benzoquinone ($n\rightarrow\pi^*$) is too weak (ε = ca. 20 mol^{-1} dm^3 cm^{-1})[8] for the origin of the 510 nm band. However, such a large red-shift (440 nm$\rightarrow$510 nm) is questionable, because the position of the $\pi^*-\sigma^*$ (Rh-O) transition band is insensitive to the axial ligation.[7] At present, the origin of the 510 nm band is unclear.

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3) Crystal Data for **2**: $Rh_2O_{10}C_{26}H_{40}$, F.W.=718.41, triclinic, space group $P\bar{1}$, a=9.862(4), b=11.745(6), c=15.162(8) Å, α=110.26(3), β=101.52(3), γ=98.91(3)°, V=1565.7(14)Å^3, Z=2, D_m=1.545, D_c=1.524 g cm^{-3}, μ(Mo-Kα)=10.8 cm^{-1}, crystal dimensions 0.35×0.30×0.20 mm^3. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using a graphite-monochromated Mo-Kα radiation. A total of 5102 reflections were collected, of which independent 3956 reflections with $I>3\sigma(I)$ were considered as observed. The structure was solved by heavy atom method and refined by full-matrix least-square methods. The refinement converged at R=0.030 and R_w=0.033. All the calculations were performed on a Micro-VAX II computer with the SDP program package.

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