Chain Compounds of Rhodium(II) Trifluoroacetate Linked by *p*-Quinone $[Rh_2(O_2CCF_3)_4(p\text{-}Q)]_n$, *p*-Q=1,4-Benzoquinone, 1,4-Naphthoquinone, and 2,3-Dimethyl-1,4-benzoquinone

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A series of chain complexes of rhodium(II) trifluoroacetate, $[Rh_2(O_2CCF_3)_4(p\text{-}Q)]_n$ (*p*-Q = 1,4-benzoquinone (1,4-bq), 1,4-naphthoquinone (1,4-nq), and 2,3-dimethyl-1,4-benzoquinone (2,3-dmbq)) have been prepared. The chain structures were confirmed by the X-ray structure analyses. The carbonyl oxygens of the *p*-quinones are coordinated to the Rh_2 centers with the distances of 2.248(5) (for *p*-Q = 1,4-bq), 2.248(3) (for *p*-Q = 1,4-nq), and 2.247(9) Å (for *p*-Q = 2,3-dmbq), respectively. The bridging mode of the *p*-quinone was discussed in relation to the substituent effect of CF_3 group on the carboxylate.

Tetra-μ-carboxylato dimetal complexes ($M_2(O_2CR)_4$) with a metal–metal bond have been fascinating many chemists because of their characteristic properties in optics, magnetism, and electrochemistry.[1] Recently, some investigations have been made to use the dimetal complexes for producing one-dimensional magnetic substances in combination with nitronyl nitroxide radicals, NITR (2-R-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl-3-oxide).[2,3] Cotton et al. prepared TCNE (tetracyanoethylene) bridged polymer complexes, $\{[Rh_2(O_2CCF_3)_4]_2(TCNE)\}_n \cdot 2n$(benzene) and $[Rh_2(O_2CMe)_4(TCNE)]_n \cdot n$(solvent) (solvent=benzene and benzene+*m*-xylene).[4] The use of electron acceptor TCNE as the bridging ligand for the Rh_2 dimers is unique for development of new materials. We have been studying chain complexes using a kind of oxidizing agent (i.e., electron acceptors), *p*-quinones, as the bridging ligands for $M_2(O_2CR)_4$ dimers.[5—7] We previously reported a chain complex $[Rh_2(O_2CCMe_3)_4(1,4\text{-bq})]_n$ (**1**) (1,4-bq=1,4-benzoquinone), in which 1,4-bq works as a bifunctional bridging ligand with its carbonyl group and C=C double bond.[6] In order to examine whether this bridging mode of *p*-quinone is general or not, in the combination with $Rh_2(O_2CR)_4$ dimers, rhodium(II) trifluoroacetate $Rh_2(O_2CCF_3)_4$ was used for the reaction with *p*-quinones in this study. We present chain complexes $[Rh_2(O_2CCF_3)_4(p\text{-}Q)]_n$ (*p*-Q=*p*-quinone; 1,4-bq, 1,4-nq (1,4-naphthoquinone), and 2,3-dmbq (2,3-dimethyl-1,4-benzoquinone)). In these complexes, the *p*-quinones link the Rh_2 dimers only by their two carbonyl groups. The substituent effect of R on carboxylate will be discussed to explain the differences in the bridging mode of the *p*-quinone for $Rh_2(O_2CR)_4$, R = CMe_3 and CF_3.

Experimental

Preparations of Complexes. Rhodium(II) trifluoroacetate ($Rh_2(O_2CCF_3)_4$) was prepared by nearly the same way as that of the literature.[8] $Rh_2(O_2CCF_3)_4$ is air-sensitive enough to allow easily axial coordinations of water molecules which were removed by heating under vacuum. The anhydrous one is green and turns blue on the water coordinations.

1,4-bq and 1,4-nq were obtained from Wako Chemical Co. 2,3-dmbq was prepared by a literature method.[9]

$[Rh_2(O_2CCF_3)_4(1,4\text{-bq})]_n$ (2). A solution of 1,4-bq (6 mg, 0.056 mmol) in benzene (5 ml) was added to a solution of $Rh_2(O_2CCF_3)_4$ (32 mg, 0.049 mmol) in benzene (5 ml) under Ar, and the mixture was stirred for 2 h at room temperature. The precipitation was filtered off, washed with benzene, and dried under vacuum to give a brown powder. The yield was 23 mg. Found: C, 21.96; H, 0.81%. Calcd for $C_7H_2F_6RhO_5$: C, 21.95; H, 0.53%.

$[Rh_2(O_2CCF_3)_4(1,4\text{-nq})]_n$ (3). This compound was obtained as an yellowish brown powder by the reaction of $Rh_2(O_2CCF_3)_4$ (30 mg, 0.046 mmol) with 1,4-nq (8 mg, 0.051 mmol) in benzene using a method similar to that of **2**. The yield was 19 mg. Found: C, 26.85; H, 0.87%. Calcd for $C_9H_3F_6RhO_5$: C, 26.49, H, 0.74%.

$[Rh_2(O_2CCF_3)_4(2,3\text{-dmbq})]_n$ (4). This compound was obtained as a brown powder by the reaction of $Rh_2(O_2CCF_3)_4$ (30 mg, 0.046 mmol) with 2,3-dmbq (7 mg, 0.051 mmol) in benzene using a method similar to that of **2**. The yield was 15 mg. Found: C, 24.32; H, 1.12%. Calcd for $C_8H_4F_6RhO_5$: C, 24.20; H, 1.02%.

The complexes **2** and **4** are air-sensitive enough to turn bluish, although the complex **3** is relatively stable. They were stored in the Ar atmosphere.

Measurements. Elemental analyses for carbon and hydrogen were carried out using Yanaco CHN CORDER MT-5. The electronic spectra were measured with a Shimadzu UV-3100 spec-

trophotometer.

X-Ray Crystal Structure Analysis. Crystals suitable for a single-crystal X-ray structure determination were obtained from benzene solution as those with benzene molecules: $[Rh_2(O_2CCF_3)_4(1,4\text{-bq})]_n\cdot 3n$(benzene) (**2**·3*n*(benzene)), $[Rh_2(O_2CCF_3)_4(1,4\text{-nq})]_n\cdot n$(benzene) (**3**·*n*(benzene)), and $[Rh_2(O_2CCF_3)_4(2,3\text{-dmbq})]_n\cdot 1.5n$(benzene) (**4**·1.5*n*(benzene)) by a slow diffusion technique using H-shaped tube. Diffraction data were collected on Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation at 25±1°C. Crystal data and details concerning data collection are given in Table 1. The lattice constants were determined by a least-squares refinement based on 25 reflections with $20\leq 2\theta\leq 30°$. The intensity data were corrected for Lorentz-polarization effects. The structures were solved by direct methods. Refinements were carried out by the full-matrix least-squares methods. All of the non-hydrogen atoms except for disordered solvent molecules were refined with anisotropic thermal parameters. Hydrogen atoms were fixed at their calculated positions. The weighting scheme, $w=1/[\sigma^2(|F_o|)+(0.02|F_o|)^2+1.0]$, was employed. The final discrepancy factors, $R=\sum||F_o|-|F_c||/\sum|F_o|$ and $R_w=[\sum w(|F_o|-|F_c|)^2/\sum|F_o|^2]^{1/2}$, are listed in Table 1. All of the calculations were carried out on a VAX station 4000 90A computer using a MolEN program package.[10] The atomic coordinates and thermal parameters of non-hydrogen atoms are listed in Table 2. The anisotropic thermal parameters of non-hydrogen atoms, the atomic coordinates and temperature factors of hydrogen atoms, and the F_o-F_c tables were deposited as Document No. 69070 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

The reactions of $Rh_2(O_2CCF_3)_4$ with slight excess of 1,4-bq, 1,4-nq, and 2,3-dmbq in benzene gave the compounds of formulae with $Rh_2(O_2CCF_3)_4:p\text{-}Q=1:1$, which are consistent with those for the chain complexes $[Rh_2(O_2CCF_3)_4(p\text{-}Q)]_n$. The chain structures were confirmed by the X-ray structure determinations. The crystal structures of $[Rh_2(O_2CCF_3)_4(1,4\text{-bq})]_n\cdot 3n$(benzene) (**2**·3*n*(benzene)), $[Rh_2(O_2CCF_3)_4(1,4\text{-nq})]_n\cdot n$(benzene) (**3**·*n*(benzene)), and $[Rh_2(O_2CCF_3)_4(2,3\text{-dmbq})]_n\cdot 1.5n$(benzene) (**4**·1.5*n*(benzene)) are shown in Figs. 1, 2, and 3, respectively. In all the cases, the chain structures with alternated arrangements of $Rh_2(O_2CCF_3)_4$ dimers and *p*-quinone molecules are formed by the axial coordinations of carbonyl oxygens of the *p*-quinones to the

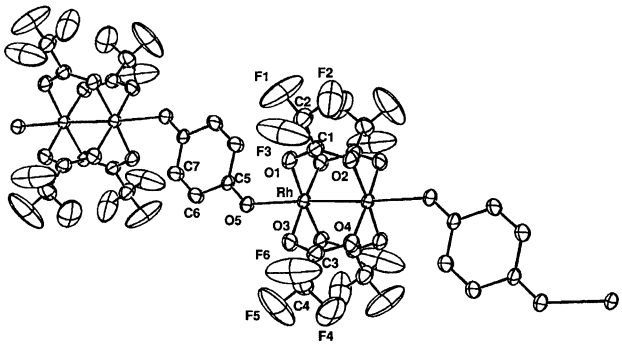


Fig. 1. ORTEP view of $[Rh_2(O_2CCF_3)_4(1,4\text{-bq})]_n\cdot 3n$(benzene) (**2**·3*n*(benzene)). Benzene molecules are omitted for clarity.

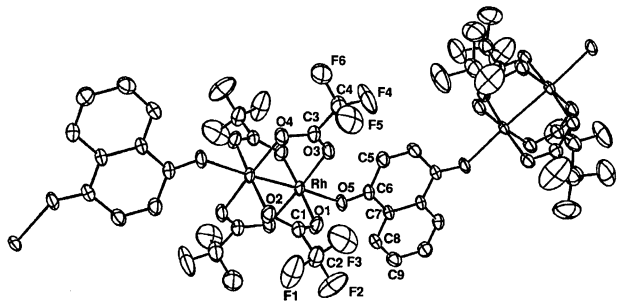


Fig. 2. ORTEP view of $[Rh_2(O_2CCF_3)_4(1,4\text{-nq})]_n\cdot n$(benzene) (**3**·*n*(benzene)). Benzene molecules are omitted for clarity.

Table 1. Crystal Data and Data Collection Details

	2·3*n*(benzene)	**3**·*n*(benzene)	**4**·1.5*n*(benzene)
Formula	$Rh_2F_{12}O_{10}C_{32}H_{22}$	$Rh_2F_{12}O_{10}C_{24}H_{12}$	$Rh_2F_{12}O_{10}C_{25}H_{17}$
F.W.	1000.34	894.17	911.20
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*m*	*C*2/*m*
a/Å	9.137(3)	14.427(3)	17.783(9)
b/Å	20.768(2)	20.995(2)	21.023(6)
c/Å	20.207(6)	10.157(2)	11.593(7)
β/°	96.38(1)	92.23(1)	128.60(2)
V/Å^3	3810(2)	3074(1)	3387(3)
Z	4	4	4
D_c/g cm^{-3}	1.74	1.93	1.79
Crystal size/mm	0.42 × 0.40 × 0.08	0.43 × 0.42 × 0.20	0.31 × 0.22 × 0.14
μ(Mo $K\alpha$)/cm^{-1}	9.59	11.77	10.70
2θ range/°	2.0—61.0	2.0—49.0	2.0—50.0
No. of reflections measured	6103	2790	3054
No. of unique reflections with $I>3\sigma(I)$	2969	2128	1464
R	0.056	0.031	0.063
R_w	0.066	0.041	0.070

Table 2. Fractional Positional Parameters and Thermal Parameters of Non-Hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^2 [a]
2·3*n*(benzene)				
Rh	0.47833(6)	0.44404(2)	0.51099(3)	3.212(9)
F1	0.0226(9)	0.5134(5)	0.5739(6)	16.0(3)
F2	0.0836(9)	0.6018(4)	0.5753(6)	17.6(3)
F3	0.156(1)	0.5456(8)	0.6474(4)	19.8(4)
F4	0.8275(9)	0.5584(5)	0.6899(4)	13.2(2)
F5	0.782(1)	0.4707(5)	0.7101(4)	18.1(3)
F6	0.640(1)	0.5385(8)	0.7250(4)	19.4(5)
O1	0.2922(6)	0.4708(2)	0.5509(3)	4.2(1)
O2	0.3331(6)	0.5761(2)	0.5306(3)	4.2(1)
O3	0.5946(6)	0.4561(2)	0.6022(3)	4.3(1)
O4	0.6349(6)	0.5615(2)	0.5814(3)	4.3(1)
O5	0.4515(6)	0.3393(2)	0.5349(3)	4.1(1)
C1	0.2643(9)	0.5297(4)	0.5525(4)	3.8(2)
C2	0.134(1)	0.5487(4)	0.5879(5)	5.2(2)
C3	0.6424(9)	0.5111(4)	0.6164(5)	4.1(2)
C4	0.720(1)	0.5192(5)	0.6868(5)	5.5(2)
C5	0.3567(8)	0.2983(3)	0.5179(4)	3.4(1)
C6	0.384(1)	0.2307(4)	0.5359(5)	5.6(2)
C7	0.285(1)	0.1855(4)	0.5185(5)	5.4(2)
C8	0.500	0.337(1)	0.750	10.5(7)[b]
C9	0.580(2)	0.3052(8)	0.7095(7)	10.0(4)
C10	0.585(2)	0.2403(8)	0.7095(7)	9.5(4)
C11	0.500	0.2076(9)	0.750	8.9(5)[b]
C12	0.049(2)	0.6536(7)	0.3883(9)	10.9(5)
C13	0.140(2)	0.6970(8)	0.4163(8)	9.7(4)
C14	0.108(2)	0.7606(7)	0.4062(7)	9.6(4)
C15	−0.005(2)	0.7778(8)	0.3664(8)	13.2(5)
C16	−0.099(2)	0.735(1)	0.337(1)	17.1(7)
C17	−0.071(2)	0.6703(9)	0.350(1)	14.0(6)
3·*n*(benzene)				
Rh	0.70592(3)	0.29446(2)	0.03829(4)	2.921(7)
F1	0.6094(4)	0.2086(2)	−0.4262(4)	10.6(1)
F2	0.5242(3)	0.2775(3)	−0.3516(5)	9.8(1)
F3	0.6484(5)	0.3039(3)	−0.4219(5)	12.6(2)
F4	0.9198(4)	0.4307(2)	−0.1366(6)	10.8(1)
F5	0.9097(4)	0.3710(3)	−0.3020(5)	10.5(1)
F6	1.0162(3)	0.3569(2)	−0.1570(5)	7.8(1)
O1	0.6351(3)	0.2929(2)	−0.1392(4)	4.02(8)
O2	0.7171(3)	0.2089(2)	−0.2105(4)	3.91(8)
O3	0.7997(3)	0.3523(2)	−0.0462(4)	3.95(8)
O4	0.8833(3)	0.2690(2)	−0.1167(4)	4.06(8)
O5	0.6166(3)	0.3735(1)	0.1122(4)	3.59(7)
C1	0.6582(4)	0.2526(2)	−0.2217(5)	3.6(1)
C2	0.6104(5)	0.2594(3)	−0.3586(6)	5.1(1)
C3	0.8643(4)	0.3272(2)	−0.1051(6)	3.7(1)
C4	0.9275(5)	0.3729(3)	−0.1765(7)	5.6(2)
C5	0.7040(4)	0.4685(2)	0.1014(6)	3.7(1)
C6	0.6193(4)	0.4318(2)	0.1247(5)	3.00(9)
C7	0.5366(3)	0.4666(2)	0.1628(5)	2.74(9)
C8	0.4565(4)	0.4338(2)	0.1958(5)	3.6(1)
C9	0.3784(4)	0.4671(3)	0.2294(6)	4.3(1)
C10	0.2636(9)	0.0623(5)	0.4188(9)	11.2(3)
C11	0.1862(8)	0.0313(5)	0.4409(8)	10.1(3)
C12	0.3466(8)	0.0336(6)	0.396(1)	14.3(5)
4·1.5n(benzene)				
Rh	0.24916(7)	0.20388(5)	0.0602(1)	4.30(2)
F1	0.2245(7)	0.1520(7)	−0.390(1)	16.5(4)
F2	0.095(1)	0.1524(9)	−0.461(1)	17.5(6)
F3	0.182(1)	0.0837(6)	−0.328(1)	22.5(6)
F4	−0.0830(8)	0.2216(8)	−0.244(2)	16.9(7)
F5	−0.0847(9)	0.294(1)	−0.357(1)	17.6(6)
F6	−0.0580(8)	0.3105(9)	−0.167(2)	21.8(7)
O1	0.2168(6)	0.1522(4)	−0.1126(8)	5.5(2)
O2	0.2171(5)	0.2391(4)	−0.2283(8)	5.3(2)
O3	0.1055(6)	0.2189(5)	−0.0574(9)	5.6(3)
O4	0.1067(5)	0.3062(5)	−0.1674(8)	5.4(3)
O5	0.2482(5)	0.1248(4)	0.1896(8)	5.0(2)
C1	0.2046(8)	0.1804(6)	−0.221(1)	5.0(3)
C2	0.179(1)	0.1403(9)	−0.345(1)	8.3(5)
C3	0.0654(9)	0.2638(7)	−0.146(1)	5.6(4)
C4	−0.041(1)	0.2713(9)	−0.237(2)	8.3(6)
C5	0.2556(8)	0.0308(6)	0.087(1)	4.9(3)
C6	0.2514(7)	0.0660(6)	0.191(1)	3.7(3)
C7	0.2480(7)	0.0319(6)	0.300(1)	3.8(3)
C8	0.2454(8)	0.0713(7)	0.403(1)	5.9(4)
C9	0.500	0.063(2)	0.500	15(2)[b]
C10	0.497(1)	0.032(1)	0.399(2)	15(1)
C11a	0.400(3)	0.000	0.931(5)	9(2)[c]
C11b	0.386(9)	0.000	0.86(1)	28(6)[c]
C12a	0.462(3)	0.052(3)	0.024(5)	15(2)[b]
C12b	0.445(5)	0.049(3)	0.896(7)	20(3)[b]
C13	0.000	0.054(2)	0.959(3)	7.2(9)[b]
C14	0.008(2)	0.039(2)	0.881(3)	20(2)

a) Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$. b) Refined with occupancy factor of 0.5. c) Refined with occupancy factor of 0.25.

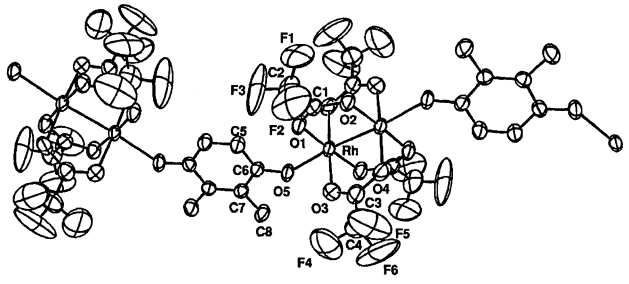


Fig. 3. ORTEP view of $[Rh_2(O_2CCF_3)_4(2,3\text{-dmbq})]_n$·1.5*n*-(benzene) (**4**·1.5*n*(benzene)). Benzene molecules are omitted for clarity.

Rh_2 dimers. The crystallographic inversion centers are located at the centers of the $Rh_2(O_2CCF_3)_4$ dimers for all the complexes. Further, 1,4-bq of **2**·3*n*(benzene) has a crystallographic inversion center, whereas 1,4-nq of **3**·*n*(benzene) and 2,3-dmbq of **4**·1.5*n*(benzene) have the crystallographic mirror planes.

Selected bond distances and angles concerning the Rh_2 cores are listed in Table 3. No remarkable difference can be recognized among the core features of these complexes. *p*-Quinones are coordinated to the dimers with the Rh–O_{ax} distances of 2.248(5) (**2**·3*n*(benzene)), 2.248(3) (**3**·*n*(benzene)), and 2.247(9) Å (**4**·1.5*n*(benzene)). These values

Table 3. Selected Bond Distance (Å) and Angles (°) Concerning Rh_2 Cores for **2**·3*n*(benzene), **3**·*n*(benzene), and **4**·1.5*n*(benzene) with Their Estimated Standard Deviations in Parentheses

2·3*n*(benzene)[a]			
Rh–Rh′	2.407(1)	Rh–O3	2.038(6)
Rh–O1	2.039(6)	Rh–O4′	2.035(5)
Rh–O2′	2.043(6)	Rh–O5	2.248(5)
O1–Rh–O3	89.0(2)	O2′–Rh–O4′	88.7(2)
O1–Rh–O4′	91.0(2)	O1–Rh–O2′	176.0(2)
O2′–Rh–O3	91.1(2)	O3–Rh–O4′	176.1(2)
Rh′–Rh–O5	176.5(1)	Rh–O5–C5	134.2(5)
3·*n*(benzene)[b]			
Rh–Rh′	2.405(1)	Rh–O3	2.033(4)
Rh–O1	2.037(4)	Rh–O4′	2.037(4)
Rh–O2′	2.036(4)	Rh–O5	2.248(3)
O1–Rh–O3	87.4(1)	O2′–Rh–O4′	88.5(1)
O1–Rh–O4′	91.9(1)	O1–Rh–O2′	175.8(1)
O2′–Rh–O3	91.9(1)	O3–Rh–O4′	175.8(1)
Rh′–Rh–O5	176.6(1)	Rh–O5–C6	138.8(3)
4·1.5*n*(benzene)[c]			
Rh–Rh′	2.400(2)	Rh–O3	2.034(8)
Rh–O1	2.021(9)	Rh–O4′	2.046(9)
Rh–O2′	2.034(9)	Rh–O5	2.247(9)
O1–Rh–O3	87.6(4)	O2′–Rh–O4′	88.3(4)
O1–Rh–O4′	91.2(4)	O1–Rh–O2′	176.3(4)
O2′–Rh–O3	92.7(4)	O3–Rh–O4′	175.4(4)
Rh′–Rh–O5	173.8(2)	Rh–O5–C6	137(1)

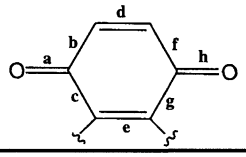
a) Primes refer to the equivalent positions $(1-x, 1-y, 1-z)$.
b) Primes refer to the equivalent positions $(3/2-x, 1/2-y, -z)$.
c) Primes refer to the equivalent positions $(1/2-x, 1/2-y, -z)$.

are comparable with those for O–donor adduct complexes of $Rh_2(O_2CCF_3)_4$ (2.220(2)—2.287(3) Å).[1] The Rh–Rh distances, 2.407(1) (**2**·3*n*(benzene)), 2.405(1) (**3**·*n*(benzene)), and 2.400(2) Å (**4**·1.5*n*(benzene)) are also in the range of those for the O–donor adducts of $Rh_2(O_2CCF_3)_4$ (2.396(2)—2.419(1) Å).[1] The Rh–O_{ax}–C(*p*-Q) bond angles are 134.2(5)—138.8(3)°, which is responsible for nonlinearity of the chain structures. There can be no significant contact of the *p*-quinone oxygen with Rh_2 core and benzene molecules other than the axial coordination seen for **2**·3*n*(benzene), **3**·*n*(benzene), and **4**·1.5*n*(benzene), respectively. The intrinsic σ character of the axial binding by the *p*-quinone oxygen on the Rh_2 core may make the Rh–O_{ax}–C(*p*-Q) bond angle attain a value rather close to 120°. However, it is noteworthy that substituents of the *p*-quinones, i.e., phenyl ring of 1,4-nq and methyl groups of 2,3-dmbq, are deposited in the open spaces generated by the nonlinear structures in order to avoid the steric repulsion between the substituent and Rh_2 core.

In Table 4, bond distances for *p*-quinone moieties are listed with the data for the free 1,4-bq, 1,4-nq, and 2,3-dmbq molecules.[11—13] In all the complexes, the C=O bonds are stretched by 0.01—0.03 Å on the coordinations. The other structural changes are small when the standard deviations are taken into account. However, these small changes seem to result from the interactions between the Rh_2 cores and *p*-quinones. Such an interaction has been observed in a chain complex $[Mo_2(O_2CCF_3)_4(9,10\text{-AQ}]_n$ (9,10-AQ=9,10-anthraquinone).[5]

We previously reported a chain complex $[Rh_2(O_2CCMe_3)_4(1,4\text{-bq})]_n$ (**1**).[6] The structure is schematically shown in Fig. 4. The most characteristic point is that the chain structure is formed by the axial coordinations of the carbonyl oxygen and C=C double bond of 1,4-bq to $Rh_2(O_2CCMe_3)_4$. The features in the diffuse reflectance spectra of the complexes[14] obtained by the reactions of 1, 4-nq and 2,3-dmbq with $Rh_2(O_2CCMe_3)_4$ are much closer to that of **1** than those of **2**—**4** (vide infra). The distinctive bands in the wavelength region 650—750 nm observed for the complexes as well as **1** may be associated with the coordinations of the C=C double bonds of the *p*-quinones to $Rh_2(O_2CCMe_3)_4$. From these facts, it seems that the C=C double bond of *p*-quinone has a general ability of the ligation to $Rh_2(O_2CCMe_3)_4$. The difference in coordination mode of *p*-quinone to Rh_2 core between the chain complexes $[Rh_2(O_2CCF_3)_4(p\text{-Q})]_n$ and $[Rh_2(O_2CCMe_3)_4(p\text{-Q})]_n$ presumably comes from the difference in rhodium metal soft-

Table 4. Bond Distances of the *p*-Quinone Moieties for **2**·3*n*(benzene), **3**·*n*(benzene), and **4**·1.5*n*(benzene) and Free 1,4-bq, 1,4-nq, and 2,3-dmbq (Å)



Complex	a	b	c	d	e	f	g	h	Ref.
2·3*n*(benzene)	1.235(8)	1.47(1)	1.45(1)	1.33(1)	1.33(1)	1.45(1)	1.47(1)	1.235(8)	This work
3·*n*(benzene)	1.230(5)	1.471(7)	1.465(7)	1.321(7)	1.403(6)	1.471(7)	1.465(7)	1.230(5)	This work
4·1.5*n*(benzene)	1.24(1)	1.46(2)	1.48(2)	1.29(2)	1.34(2)	1.46(2)	1.48(2)	1.24(1)	This work
1,4-bq	1.218(8)	1.467(6)	1.467(6)	1.312(8)	1.312(8)	1.467(6)	1.467(6)	1.218(8)	11
1,4-nq[a]	1.21	1.48	1.43	1.31	1.39	1.45	1.46	1.22	12
2,3-dmbq[b]	1.22	1.44	1.48	1.30	1.33	1.47	1.47	1.21	13

a) Estimated standard deviations (esd) for the bond lengths are not described in the literature. b) The average esd of the bond lengths is 0.006 Å.

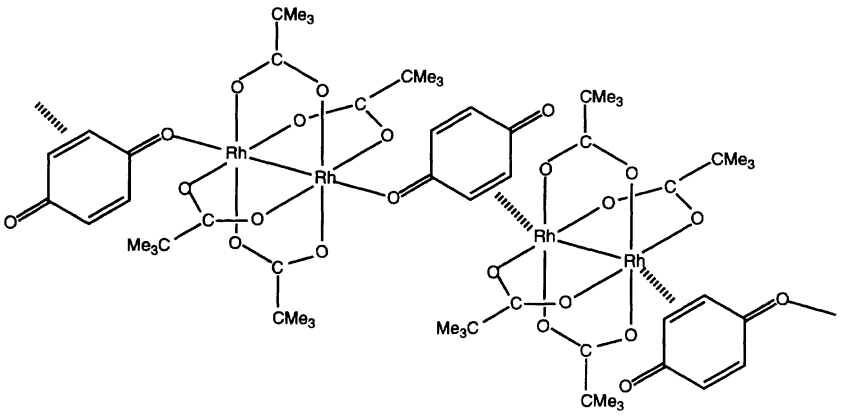


Fig. 4. Schematic drawing for $[Rh_2(O_2CCMe_3)_4(1,4\text{-bq})]_n$ (**1**).

ness influenced by substituent group R on carboxylate of $Rh_2(O_2CCR)_4$. That is, *t*-butyl group on the carboxylate increases the softness of Rh metal to enable the coordination of the C=C double bond. The effect of substituent R on the carboxylate has been investigated for the DMSO (dimethylsulfoxide) adduct complexes, $Rh_2(O_2CR)_4(DMSO)_2$ (R=CF_3, Me, Et, and Ph).[15] In the case of R=CF_3, DMSO is coordinated by O atom, but by S atom in the case of R=Me, Et, and Ph. In the complex **1**, the coordination of the C=C double bond affects the Rh_2 core more than that of the carbonyl oxygen; the Rh–Rh bond lengths are 2.403(1) Å for the Rh_2 core coordinated by the C=C double bonds and 2.375(1) Å for that by the carbonyl oxygens. The carbonyl coordinations of **2**·3*n*(benzene), **3**·*n*(benzene), and **4**·1.5*n*(benzene) are stronger than that for **1** ($Rh–O_{ax}$ = 2.289(3) Å). These results suggest that the metal softness or hardness is strongly influenced by the substituent group R of the $Rh_2(O_2CR)_4$ units.

Diffuse reflectance spectra of **2**—**4** and $Rh_2(O_2CCF_3)_4$ are shown in Fig. 5. The absorption band around 640 nm for $Rh_2(O_2CCF_3)_4$ is assigned to a $\pi^*(Rh_2)\rightarrow\sigma^*(Rh_2)$ transition.[16] It is well known that the band is quite sensitive to the axial ligation.[17] Drago et al. proposed that the axial π and σ interactions with the ligand cause the blue-shift of the band.[18] The bands are observed around 580 nm as shoulders for **2** and **3** and a peak for **4**. The spectral features in the range of 400—500 nm are complicated, perhaps due to superposition of absorption bands related to Rh_2 core and *p*-quinone molecules; the Rh_2 dimers have π(Rh–O)$\rightarrow\sigma^*$(Rh–O) absorption bands at ca. 450 nm[19] and the free *p*-quinones show the $n\rightarrow\pi^*$ transition band around 430 nm.[20]

In this study, it has been confirmed that the carbonyl oxygen of *p*-quinone has enough coordination ability to the rhodium(II) trifluoroacetate dimer to form chain complexes. Our final goal for this type of chain complex is to give rise to an electron-transfer from the dimer core to *p*-quinone on the polymer formation. Such study is in progress in our laboratory.

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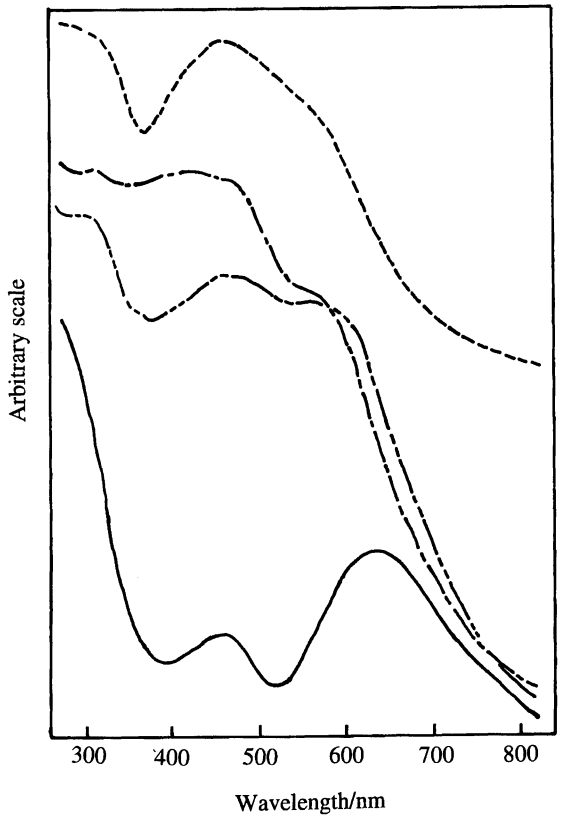

Fig. 5. Reflectance spectra of **2** (- - -), **3** (– · –), **4** (– ·· –), and $Rh_2(O_2CCF_3)_4$ (——).

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