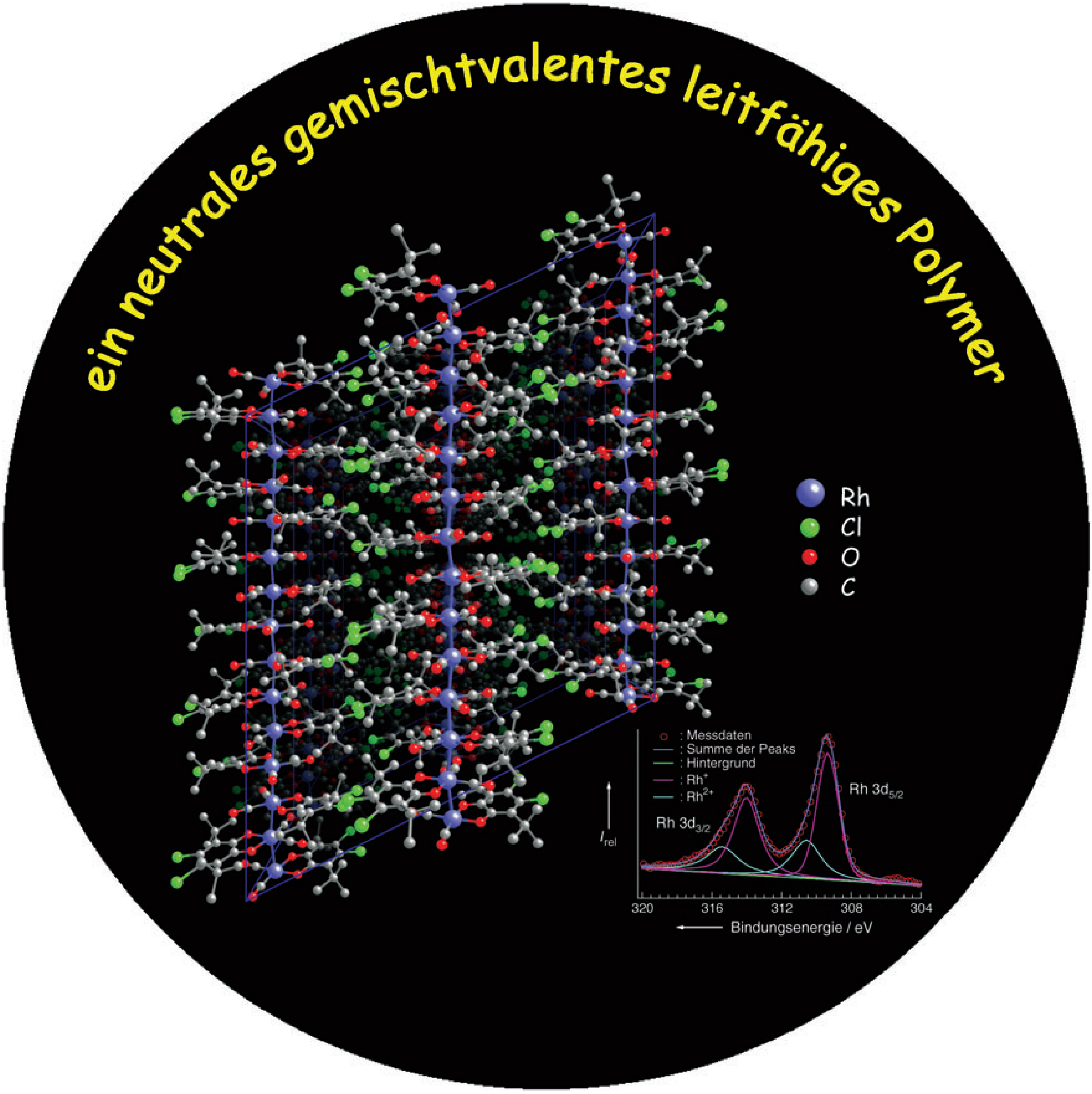
# Zuschriften



Die spektroskopischen und kristallographischen Eigenschaften eines leitfähigen gemischtvalenten Rhodium(I,II)-Semichinonato/Catecholato-Neutralkomplexes, dessen gemischtvalente Zustände durch Elektronentransfer von Rhodium-d- auf Semichinonat-π*-Orbitale entstehen, beschreiben M. Mitsumi, K. Toriumi et al. in der Zuschrift auf den folgenden Seiten.

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Conducting Materials

# A Neutral Mixed-Valent Conducting Polymer Formed by Electron Transfer between Metal d and Ligand π Orbitals**

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Recently, conducting systems that consist of a single-component molecule have attracted much attention.[1–3] These studies should develop basic technology for molecular electronic devices. Kobayashi and co-workers reported that a crystal of $[Ni(tmdt)_2]_\infty$ (tmdt = trimethylenetetrathiafulvalenedithiolate) is a single-component molecular metal with a 3D π band, which was designed on the basis of a very small HOMO–LUMO gap and crossing bands formed by the HOMO and LUMO.[1] On the other hand, many directly bonded infinite M−M chain compounds have been prepared, but a single-component molecular conductor with a metal-containing backbone has yet to be reported.[4,5]

When building such a material by the bottom-up method, frontier-orbital engineering is very important for obtaining the desired physical properties and/or functionalities. Redox-active dioxolene derivatives can create redox isomers of benzoquinone (BQ), semiquinonate ($SQ^{\bullet -}$), and catecholate ($cat^{2-}$) by two sequential one-electron transfers. Several transition-metal complexes that contain these dioxolene ligands have very close energy levels between the frontier orbitals of the metal d and dioxolene ligand π orbitals, and intramolecular electron transfer occurs between the metal and the ligand in a thermal equilibrium known as valence tautomerism.[6] On the other hand, the rhodium(I) semiquinonato complex $[Rh(3,6\text{-dbsq})(CO)_2]_\infty$ (3,6-dbsq = 3,6-di-*tert*-butyl-1,2-benzosemiquinonate) was reported to form a linear-chain structure with a direct Rh−Rh interaction.[7] Although this compound does not show valence tautomerism, the energy levels of the electron-rich rhodium(I) core and the electron-deficient semiquinonato ligand are considered to be relatively close. If the energy level of the ligand $\pi^*(SQ^{\bullet -})$ orbital can be adjusted to be close to or the same as the energy level of the 1D d band, which is comprised of metal $d_{z^2}$ orbitals, a rhodium(I,II) semiquinonato/catecholato mixed-valent state would be achieved by intramolecular electron transfer between metal and ligand (Figure 1). This approach may be a fundamental methodology for the development of novel neutral mixed-valent conducting polymers with metal-containing backbones based on metal complexes. Recently, we successfully controlled the energy level of the frontier orbitals in the metal complex by chemically modifying the ligand. Electron transfer was realized between metals and ligands, and a mixed-valent state of the directly bonded infinite M−M chain was ascertained.

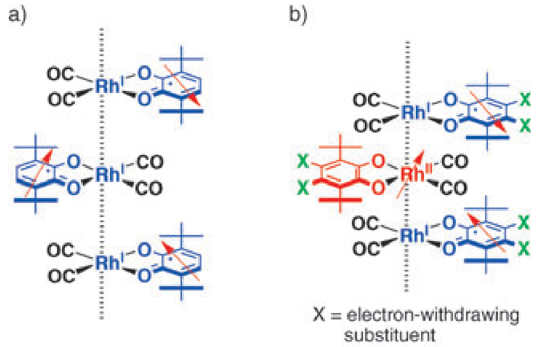

***Figure 1.*** a) Stacking of $\{Rh^+\text{-}SQ^{\bullet -}\}$ units in $[Rh(3,6\text{-dbsq})(CO)_2]_\infty$. b) Mixed stack of $\{Rh^+\text{-}SQ^{\bullet -}\}$ and $\{Rh^{2+}\text{-}cat^{2-}\}$ units.

Herein, we report the synthesis, crystal structure, and electronic properties of the novel linear-chain mixed-valent rhodium(I,II) semiquinonato/catecholato complex $[Rh(3,6\text{-dbdiox-}4,5\text{-}Cl_2)(CO)_2]_\infty$ (**1**), in which 3,6-dbdiox-4,5-$Cl_2$ indicates the 3,6-di-*tert*-butyl-4,5-dichloro-1,2-benzosemiquinonate (3,6-dbsq-4,5-$Cl_2^{\bullet -}$) or 3,6-di-*tert*-butyl-4,5-dichlorocatecholate (3,6-dbcat-4,5-$Cl_2^{2-}$) state. This compound is the first example of a neutral mixed-valent conducting polymer with a metal-containing backbone in which the mixed-valent state is formed by electron transfer between metal d and ligand π* orbitals.

Black needle crystals of **1** were obtained by a redox reaction of $[Rh_4(CO)_{12}]$ with 3,6-di-*tert*-butyl-4,5-dichloro-1,2-benzoquinone[8] in *n*-pentane.[9]

The X-ray photoelectron spectrum (XPS) of **1** exhibits broad Rh $3d_{5/2}$ and $3d_{3/2}$ signals compared to the spectrum of the rhodium(I) complex $[Rh(3,6\text{-dbsq})(CO)_2]_\infty$. The signals of **1** are well resolved into $Rh^+$ $3d_{5/2,3/2}$ and $Rh^{2+}$ $3d_{5/2,3/2}$ doublets (Figure 2), which clearly reveal that **1** exists in the mixed-valent state composed of $Rh^+$ and $Rh^{2+}$ on the rapid XPS timescale (ca. $10^{-17}$ s).[10] Furthermore, the intensity ratios of the $Rh^+$ $3d_{5/2}$/$Rh^{2+}$ $3d_{5/2}$ and $Rh^+$ $3d_{3/2}$/$Rh^{2+}$ $3d_{3/2}$ doublets are 2:1(±0.1). This suggests that the formal oxidation state of

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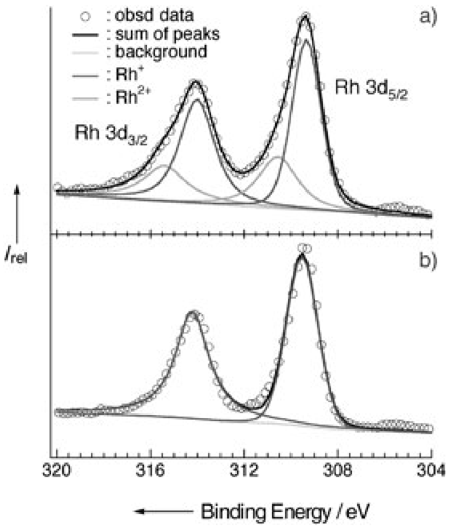

*Figure 2.* Rh $3d_{5/2}$ and Rh $3d_{3/2}$ core-level spectra for a) **1** and b) [Rh(3,6-dbsq)(CO)$_2$]$_\infty$. obsd = observed

rhodium is approximately $Rh^{1.33+}$ and the [$Rh^I$(3,6-dbsq-4,5-$Cl_2$)(CO)$_2$]/[$Rh^{II}$(3,6-dbcat-4,5-$Cl_2$)(CO)$_2$] ratio is nearly 2:1.

X-ray crystal structure analysis of **1** was performed at 302 and 56 K with synchrotron radiation (see the Experimental Section). Compound **1** crystallizes in the monoclinic space group *C*2/*c* at both temperatures. It consists solely of neutral linear chains of [Rh(3,6-dbdiox-4,5-$Cl_2$)(CO)$_2$] molecules, which form trimeric units in the linear chain at 302 K (Figure 3a). The Rh–Rh distances in the trimers (2.8685(2) and 2.8629(2) Å) are about 0.03 Å shorter than the Rh–Rh distances between them (2.8942(3) and 2.8984(3) Å). These Rh–Rh distances are approximately 0.4 Å shorter than those of $Rh^+$ complex [Rh(3,6-dbsq)(CO)$_2$]$_\infty$ (3.252(4) and 3.304(5) Å)[7] and are similar to those of $Rh^{1.5+}$ complex [{Rh(MeCN)$_4$}(BF$_4$)$_{1.5}$]$_\infty$ (2.8442(8) and 2.9277(8) Å).[12] The formation of the trimer is consistent with the formal oxidation state of $Rh^{1.33+}$ estimated from the XPS spectrum. The structural data also strongly suggests that **1** has a rhodium(I,II) mixed-valent state. The overlap of the complex molecules can be classified into two modes (Figure 3b), in which the dioxolene ligands do not directly overlap. These overlap modes alternate in the linear chain. At 56 K, the trimers in the linear chain are dimerized by shortening the Rh1–Rh1* bond to form hexameric units (Figure 4). The Rh–Rh distances in the hexamer are 2.8059(3)–2.8180(2) Å, while the Rh–Rh distance between hexamers is 2.8592(3) Å. The observed dimerization of trimers in the 1D chain originates from Peierls distortion associated with the pairing of unpaired electrons in the $d_{z^2}$ orbitals of $Rh^{2+}$ ions.[13] In the crystal structures at 302 and 56 K, no notable conformational change is observed. The C–C and C–O bond lengths of each dioxolene ligand exist in the boundary region of the semiquinonate and catecholate forms, respectively. These structural features indicate that the dioxolene ligands are either charge-localized and structurally disordered or charge-delocalized. Therefore, it is impossible to determine the oxidation state of each dioxolene ligand from the C–C and C–O bond lengths.

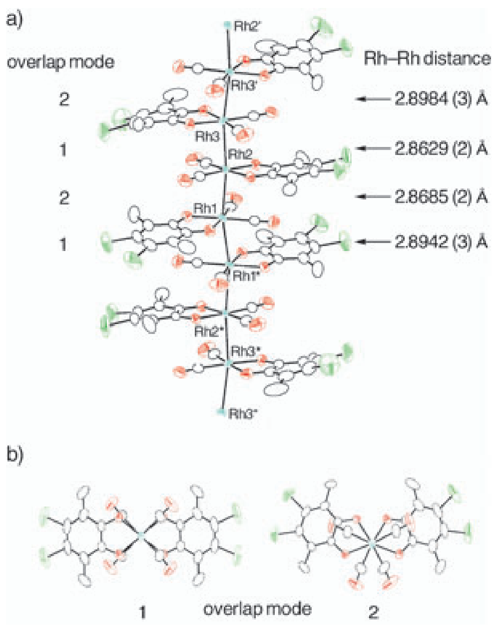

*Figure 3.* a) Linear-chain structure of **1** at 302 K. Methyl carbon atoms of the *t*Bu groups are omitted for clarity. b) Two overlap modes of the complex molecules.

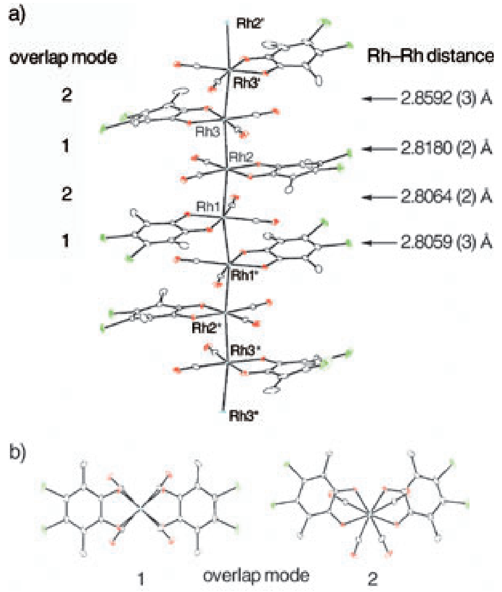

*Figure 4.* a) Linear chain structure of **1** at 56 K. Methyl carbon atoms of the *t*Bu groups are omitted for clarity. b) Two overlap modes of the complex molecules.

Figure 5 shows electronic absorption spectra of **1** in the solid state and in solution with $CH_2Cl_2$, and those of [Rh(3,6-dbsq)(CO)$_2$]$_\infty$ are shown for reference. In the solid state, [Rh(3,6-dbsq)(CO)$_2$]$_\infty$ shows a relatively intense absorption at 6700 $cm^{-1}$, which is assigned to the absorption associated with the band structure formed by $d_{z^2}$ orbitals along the linear chain.[7] The dominant feature of the absorption spectrum of **1** in the solid state is an intense, broad absorption band that extends from 15000 $cm^{-1}$ to the IR region. This broad

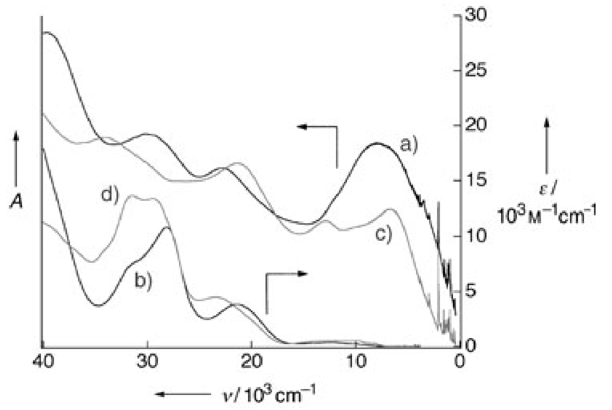

*Figure 5.* Electronic absorption spectra of **1** in the solid state (KBr pellet) (a) and in solution with $CH_2Cl_2$ (b) and of $[Rh(3,6\text{-dbsq})(CO)_2]_\infty$ in the solid state (KBr pellet) (c) and in solution with $CH_2Cl_2$ (d).

absorption band probably consists of several overlapping bands, including the intervalence charge-transfer transitions of $Rh^{2+}\leftarrow Rh^{+}$ and/or $\pi^*(SQ^{\bullet-})\leftarrow\pi^*(Cat^{2-})$[14] along with the absorption associated with the band structure formed by $d_{z^2}$ orbitals, as observed in $[Rh(3,6\text{-dbsq})(CO)_2]_\infty$. On the other hand, the absorption spectrum of a solution of **1** in $CH_2Cl_2$ is quite similar to that observed for $[Rh(3,6\text{-dbsq})(CO)_2]_\infty$ in the same solvent, and this indicates that **1** exists as a discrete rhodium(I) semiquinonato complex in solution with $CH_2Cl_2$.

Single-crystal electrical resistivity $\rho$ of **1** along the 1D chain direction was measured in the temperature range 80–300 K by a four-probe technique (Figure 6). Compound **1** shows significant electrical conductivity ($\sigma = 17$–$34\ S\,cm^{-1}$) at room temperature in spite of its neutral molecular character. This high electrical conductivity also clearly demonstrates that the rhodium atoms in **1** are in the mixed-valent state. The temperature dependence of the electrical conductivity confirms semiconducting behavior, and the activation energies $E_a$ in the high- and low-temperature regions are 114 meV (300–179 K) and 64.4 meV (154–80 K), respectively. The increase in resistivity with decreasing temperature is attributable to dimerization of the trimers. The resistivity of **1** shows significant hysteresis in the temperature range of 161–275 K, but the origin of the hysteresis is unclear.

The effective magnetic moment $\mu_{eff}$ of **1** at 300 K is 1.61 $\mu_B$, which is smaller than the theoretical value of 1.73 $\mu_B$ for a paramagnetic isolated spin of $S = 1/2$ (see the Supporting Information).[15] The $\mu_{eff}$ value gradually decreases down to 208 K, shows a rounded hump around 208–172 K, and then decreases to 1.22 $\mu_B$ at 5.0 K. This value is slightly smaller than that of 1.41 $\mu_B$ expected when two $Rh^{2+}$ spins become a spin singlet and only four semiquinonato spins exist as magnetically isolated spins in a hexamer unit. The Weiss constants $\theta$, based on the equation $\chi_M = C/(T-\theta)$, are $-59$ K (300–208 K) and $-21.6$ K (176–52 K), which suggest an antiferromagnetic interaction between the unpaired spins. This complicated magnetic behavior is attributed to either a $Rh^{2+}$ ion or a semiquinonato ligand in the rhodium complex unit with a spin of $S = 1/2$.

The electronic structure of **1** can be estimated from these experimental results as follows: At room temperature, the 1D band formed by the $d_{z^2}$ orbitals of **1** has one unpaired electron per trimer and exhibits significant conductivity. As the temperature is lowered, the trimers dimerize and the unpaired electrons pair, which lowers the conductivity.

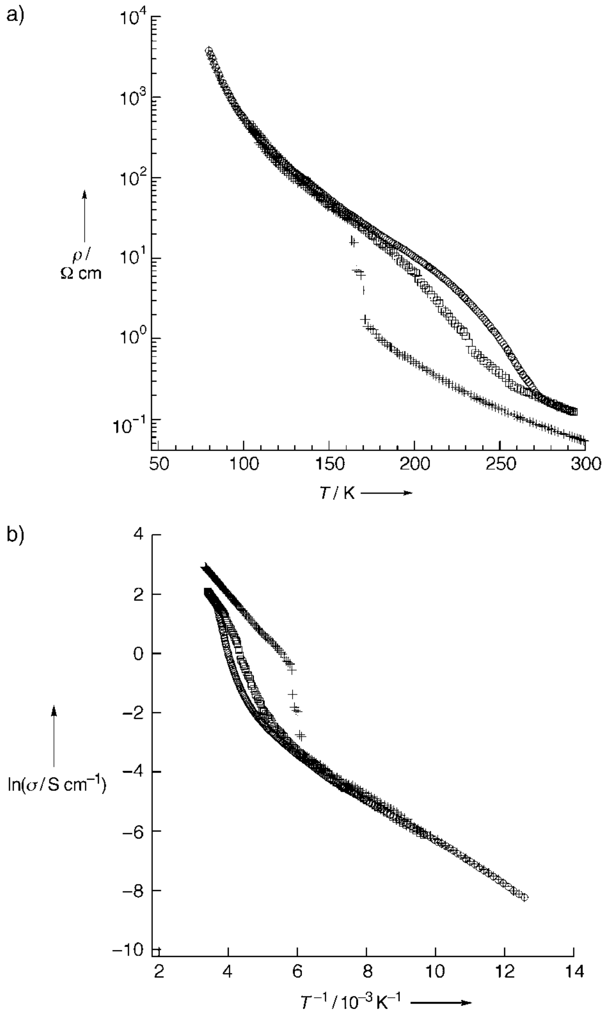

*Figure 6.* a) Temperature dependence of electrical resistivity $\rho$ of **1** measured along the 1D chain direction: 1st cooling (+), 1st heating (○), 2nd cooling (□). b) Temperature dependence of electrical conductivity $\sigma$ of **1**.

In conclusion, we have reported the first neutral linear-chain mixed-valent rhodium(I,II) semiquinonato/catecholato complex **1**, in which the mixed-valent state is realized by electron transfer between metal d and semiquinonate $\pi^*$ orbitals. This compound exhibits high conductivity (17–34 $S\,cm^{-1}$) at room temperature in spite of its being a neutral molecule. Tuning of the energy levels between the metal d and ligand $\pi$ orbitals would be expected to facilitate the control of electron transfer between metal and ligand by external factors, such as light, heat, and/or pressure. Therefore, this research offers opportunities for the development of novel neutral conducting polymers based on metal complexes in which the solid-state properties could be changed by metal–ligand electron transfer induced by such external fields. Further investigations are currently underway to produce a variety of the mixed-valent rhodium(I,II) semiquinonato/catecholato compounds by using frontier-orbital control.

## Experimental Section

**1** was prepared by a procedure similar to a literature method.[9] $[Rh_4(CO)_{12}]$ (54 mg, 0.072 mmol) and 3,6-di-*tert*-butyl-4,5-dichloro-1,2-benzoquinone[8] (96 mg, 0.33 mmol) were dissolved in *n*-pentane at 35 °C. After slowly cooling to −5 °C, black needle crystals of **1** separated from the solution. These crystals were collected by filtration and washed with *n*-pentane: yield 75 mg (58 %). Elemental analysis (%) calcd for $C_{16}H_{18}Cl_2O_4Rh$: C 42.88, H 4.05, Cl 15.82; found: C 42.68, H 3.97, Cl 15.64; UV/Vis/NIR (KBr pellet): $\lambda_{max}=$ 251, 334, 439, 1270 nm; UV/Vis/NIR ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon_M$) = 317 (sh, 7460), 356 (10 800), 468 (3830), 818 (378), 990 (sh, 238), 1160 nm (sh, 119).

X-ray crystallography for **1**: A single crystal was mounted on a carbon fiber attached to a closed-cycle helium cryostat. Data were collected at 302 and 56 K, under vacuum to measure reflection intensity accurately by reducing air-scattering background, with synchrotron radiation (20.03 keV ($\lambda = 0.6188$ Å) at 302 K and 21.99 keV ($\lambda = 0.5638$ Å) at 56 K) and a MAC Science low-temperature vacuum X-ray camera equipped with an imaging plate (IP) area detector in the BL02B1 beamline at SPring-8. The frames were indexed and the reflections integrated with DENZO and subsequently scaled with SCALEPACK.[16a] An empirical correction for absorption anisotropy was applied to all intensity data by using PLATON-MULABS.[16b] The structure was solved by direct methods (SIR97)[17a] and refined by full-matrix least-squares techniques on $F^2$ (SHELXL-97).[17b] All non-hydrogen atoms were anisotropically refined, while all hydrogen atoms were placed at their idealized positions but not refined. All calculations were performed with the teXsan crystallographic software package.[17c]

Crystal data for **1** at 302 K: $C_{16}H_{18}Cl_2O_4Rh$, $M_r = 448.13$, black needles, 0.330 × 0.065 × 0.020 mm, monoclinic, space group $C2/c$, $a = 31.696(1)$, $b = 11.142(1)$, $c = 34.317(1)$ Å, $\beta = 116.030(1)°$, $V = 10\,890.0(11)$ Å$^3$, $Z = 24$, $\rho_{calcd} = 1.640$ g cm$^{-3}$, $F(000) = 5400$, $\mu$-(0.6188 Å) = 0.803 mm$^{-1}$, $2\theta_{max} = 52.46°$. 15 811 reflections were measured, of which 10 533 were unique ($R_{int} = 0.0399$). $wR2 = 0.1001$, $S = 0.921$ (all data), $R1 = 0.0363$ (10 533 reflections with $I > 2\sigma(I)$), 622 parameters, min./max. residual electron density −1.080/0.821 e A$^{-3}$, min./max. transmission 0.94227/0.95022.

Crystal data for **1** at 56 K: $C_{16}H_{18}Cl_2O_4Rh$, $M_r = 448.13$, black needles, 0.300 × 0.075 × 0.045 mm, monoclinic, space group $C2/c$, $a = 31.644(1)$, $b = 10.990(1)$, $c = 33.683(1)$ Å, $\beta = 116.373(1)°$, $V = 10\,494.7(11)$ Å$^3$, $Z = 24$, $\rho_{calcd} = 1.702$ g cm$^{-3}$, $F(000) = 5400$, $\mu$-(0.5638 Å) = 0.632 mm$^{-1}$, $2\theta_{max} = 60.46°$. 28 574 reflections were measured, of which 22 583 were unique ($R_{int} = 0.0312$). $wR2 = 0.1282$, $S = 1.056$ (all data), $R1 = 0.0473$ (22 583 reflections with $I > 2\sigma(I)$), 622 parameters, min./max. residual electron density −2.640/5.151 e A$^{-3}$, min./max. transmission 0.91585/0.97378. CCDC-267426 and -267427 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

XPS data were obtained on a VG ESCALAB 220i-XL spectrometer equipped with nonmonochromatized $Mg_{K\alpha}$ radiation (1253.6 eV). The carbon 1s binding energy (284.6 eV) was used to calibrate the binding energy. Curve-fitting analysis was performed with the iterative least-squares computer program XPSPEAK41 by using a combination of Gaussian and Lorentzian line shapes. Direct-current electrical conductivity measurements were made on several single crystals of **1** by using a four-probe technique. Magnetic susceptibility of **1** was measured with a Quantum Design MPMS-5SH SQUID magnetometer.

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