© 1998 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, **71**, 1811—1816 (1998)

Chain Compounds of Molybdenum(II) Trifluoroacetate Linked by *p*-Quinones $[Mo_2(O_2CCF_3)_4(p\text{-quin})]_n$, *p*-quin = 9,10-anthraquinone, 2,6-dimethyl-1,4-benzoquinone, and 1,4-naphthoquinone

Makoto Handa,* Hiroki Matsumoto, Daisuke Yoshioka, Ryoji Nukada,† Masahiro Mikuriya,*,† Ichiro Hiromitsu, and Kuninobu Kasuga

Department of Material Science, Interdisciplinary Faculty of Science and Engineering, Shimane University,
Nishikawatsu, Matsue 690-8504

†Department of Chemistry, School of Science, Kwansei Gakuin University, Uegahara, Nishinomiya 662-8501

(Received January 19, 1998)

A series of chain complexes of molybdenum(II) trifluoroacetate linked by *p*-quinones, $[Mo_2(O_2CCF_3)_4(p\text{-quin})]_n$, *p*-quin = 9,10-anthraquinone (9,10-aq), 2,6-dimethyl-1,4-benzoquinone (2,6-dmbq), and 1,4-naphthoquinone (1,4-nq) have been prepared. The X-ray structure analyses showed that the carbonyl oxygens of the *p*-quinones are coordinated to the Mo_2 dimers with distances of 2.478(6) and 2.532(5) Å (for 9,10-aq), 2.619(9) and 2.596(10) Å (for 2,6-dmbq), and 2.522(8) Å (for 1,4-nq), respectively. The Mo–Mo bond distances are 2.107(1)—2.117(1)Å, which are slightly longer than that of $Mo_2(O_2CCF_3)_4$ (2.090(4) Å). Elongation of the C=O and C=C bonds of the 9,10-aq and 2,6-dmbq molecules on the coordination has been observed, but the bond distances of the coordinated and uncoordinated 1,4-nq molecules are similar to each other. The difference is discussed in terms of the oxidizing abilities and the symmetries of the *p*-quinones.

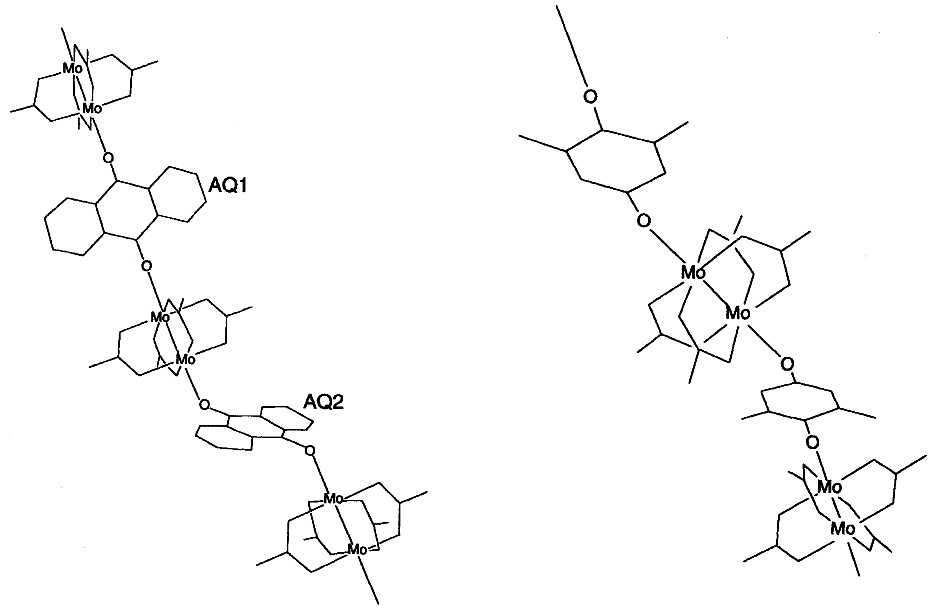
There have been a great number of studies on tetra(μ-carboxylato)dimetal complexes with a direct metal–metal bond.[1] The unique properties derived from the metal–metal bond now attract many chemists from the standpoints of application of the complexes as building blocks for new conducting or magnetic materials.[2—4] Some polymeric complexes of $M_2(O_2CR)_4$ coordinated by nitrogen donors such as pyrazine, 4,4′-bipyridine, and phenazine have been reported.[2] The π-conjugated system has been proved to be suitable for such materials in the polymeric chain complexes of metal porphyrins or phthalocyanines bridged by the ligands.[5] Recently, electron acceptors such as TCNE (tetracyanoethylene), TCNQ (7,7,8,8-tetracyanoquinodimethane), and 2,5-DM-DCNQI (2,5-dimethyl-*N*,*N*′-dicyano-1,4-benzoquinone diimine) have been used as bridging ligands in combination with $M_2(O_2CR)_4$ to give hybrid donor/acceptor polymers incorporating metal–metal bonds.[4] We also have been studying chain complexes using electron-accepting *p*-quinones as the bridging ligands of $M_2(O_2CR)_4$ dimers.[6] In the preliminary accounts,[6a,6c] we presented the crystal structures of chain complexes $[Mo_2(O_2CCF_3)_4(9,10\text{-aq})]_n$ (**1**) (9,10-aq = 9,10-anthraquinone) and $[Mo_2(O_2CCF_3)_4(2,6\text{-dmbq})]_n$ (**2**) (2,6-dmbq = 2,6-dimethyl-1,4-benzoquinone), the structures of which are schematically drawn in Fig. 1. The most characteristic point of the structures is elongation of the C=O bonds of the *p*-quinone moieties caused by their coordination to the Mo_2 centers. The structural change is more noticeable for **2**. It is assumed that the degree of the bond elongation would be correlated to the oxidizing abilities of the *p*-quinones; the redox potentials (in acetonitrile) of the first reduction for 9,10-aq[7] and 2,6-dmbq[8] are −0.98 and −0.66 V (vs. SCE), respectively. To bear out this assumption, we prepared the same type of chain complex of 1,4-naphthoquinone (1,4-nq), $[Mo_2(O_2CCF_3)_4(1,4\text{-nq})]_n$ (**3**) in addition to the complexes **1** and **2**; the redox potential of 1,4-nq[9] is −0.685 V (vs. SCE) in acetonitrile. In this report, we will discuss the bonding features of the *p*-quinone moieties of the chain complexes, considering the oxidizing ability and molecular symmetry of each *p*-quinone.

Experimental

Preparations of Complexes. Molybdenum(II) trifluoroacetate ($Mo_2(O_2CCF_3)_4$) was prepared by a method described in the literature.[10] The quinones 9,10-aq and 1,4-nq were obtained from Wako Chem. Co. and 2,6-dmbq from Aldrich Chem. Co.

$[Mo_2(O_2CCF_3)_4(9,10\text{-aq})]_n$ (1). A solution of 9,10-aq (18 mg, 0.086 mmol) in dry benzene (10 cm^3) was added to a solution of $Mo_2(O_2CCF_3)_4$ (50 mg, 0.078 mmol) in dry benzene (10 cm^3) under argon. After the solution was stirred for 1 h at room temperature, the precipitate was filtered, washed with benzene, and dried under a vacuum to give an orange powder. The yield was 29.0 mg. Anal. Found: C, 31.16; H, 0.97%. Calcd for $C_{22}H_8F_{12}Mo_2O_{10}$: C, 31.01; H, 0.95%.

$[Mo_2(O_2CCF_3)_4(2,6\text{-dmbq})]_n$ (2). This compound was obtained as a pale brown powder by the reaction of $Mo_2(O_2CCF_3)_4$ (50 mg, 0.078 mmol) with 2,6-dmbq (12 mg, 0.088 mmol) in benzene using a method similar to that of **1**. The yield was 21.1 mg. Anal. Found: C, 24.76; H, 1.05%. Calcd for $C_{16}H_8F_{12}Mo_2O_{10}$: C, 24.64; H, 1.03%.



(a) (b)

Fig. 1. Schematic illustrations for the chain structures of **1** (a) and **2** (b). Fluorine and hydrogen atoms are not depicted in the illustrations.

$[Mo_2(O_2CCF_3)_4(1,4\text{-nq})]_n$ (3). This compound was obtained as a brown powder by the reaction of $Mo_2(O_2CCF_3)_4$ (50 mg, 0.078 mmol) with 1,4-nq (14 mg, 0.089 mmol) in benzene using a method similar to that of **1**. The yield was 22.3 mg. Anal. Found: C, 26.77; H, 0.73%. Calcd for $C_{18}H_6F_{12}Mo_2O_{10}$: C, 26.95; H, 0.75%.

Measurements. Elemental analyses for carbon and hydrogen were done using a Yanako CHN CORDER MT-5. The electronic spectra were measured with a Shimadzu UV-3100 spectrophotometer. The magnetic susceptibilities were measured at room temperature and corrected for the diamagnetism of the constituent atoms using Pascal's constants.[11] The effective magnetic moments were calculated from the equation $\mu_{\text{eff}} = 2.828\sqrt{\chi_A T}$, where χ_A is the atomic magnetic susceptibility.

X-Ray Crystal Structure Analysis. Crystals of $[Mo_2(O_2CCF_3)_4(9,10\text{-aq})]_n$ (**1**), $[Mo_2(O_2CCF_3)_4(2,6\text{-dmbq})]_n$ (**2**), and $[Mo_2(O_2CCF_3)_4(1,4\text{-nq})]_n\cdot nC_6H_6$ (**3**$\cdot nC_6H_6$) suitable for single-crystal X-ray structure analysis were obtained from benzene solutions by a slow diffusion technique using H-shaped tubes. Diffraction data were collected on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation at 25±1°C. Crystal data and details concerning data collection for **3**$\cdot nC_6H_6$ are given in Table 1.[12] The lattice constants were calculated 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. Refinement was done by the full-matrix least-squares methods. The non-hydrogen atoms except for disordered solvent molecules of **3**$\cdot nC_6H_6$ 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 used. The final discrepancy factors of **3**$\cdot nC_6H_6$, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_W = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$, are listed in Table 1.[12] All of the calculations were done on a VAX station 4000 90A computer using a MolEN program package.[13] The atomic coordinates with thermal parameters of non-hydrogen atoms and the selected bond distances and angles **3**$\cdot nC_6H_6$ are listed in Tables 2 and 3, respectively. The atomic coordinates with thermal parameters of non-hydrogen atoms and the selected bond distances and angles for **1** and **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 for **1**, **2**, and **3**$\cdot nC_6H_6$ were deposited as Document No. 71038 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Table 1. Crystal Data and Data Collection Details of **3**$\cdot nC_6H_6$

Formula	$Mo_2F_{12}O_{10}C_{24}H_{12}$
F.W.	878.10
Crystal system	Monoclinic
Space group	*C*2/*m*
a/Å	13.549(6)
b/Å	21.892(4)
c/Å	10.377(5)
β/°	90.77(2)
V/Å^3	3078(2)
Z	4
D_m/g cm^{-3}	1.94
D_c/g cm^{-3}	1.90
Crystal size/mm	$0.65 \times 0.45 \times 0.35$
μ(Mo $K\alpha$)/cm^{-1}	9.24
2θ range/°	1—50
No. of reflections measured	2784
No. of unique reflections with $I > 3\sigma(I)$	2207
R	0.057
R_w	0.082

Results and Discussion

The schematic illustrations for **1** and **2** are given in Fig. 1. The ORTEP view of **3**$\cdot nC_6H_6$ is shown in Fig. 2. The chain structure of **3**$\cdot nC_6H_6$ is made up by the alternating arrange-

Table 2. Fractional Positional Parameters and Thermal Parameters of Non-Hydrogen Atoms for **3**·nC$_6$H$_6$ with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^2 [a)]
Mo	0.20335(7)	0.28503(4)	0.46408(9)	3.10(2)
F1	0.109(1)	0.2115(5)	0.9257(9)	12.2(3)
F2	0.0175(7)	0.2807(7)	0.8527(9)	10.9(3)
F3	0.1549(9)	0.3020(6)	0.9233(9)	11.7(3)
F4	0.5310(6)	0.3691(4)	0.660(1)	8.2(3)
F5	0.4211(8)	0.4349(4)	0.635(1)	12.8(4)
F6	0.4157(9)	0.3810(6)	0.802 (1)	11.6(3)
O1	0.1241(5)	0.2895(3)	0.6370(7)	3.8(2)
O2	0.2977(6)	0.3529(3)	0.5471(8)	4.0(2)
O3	0.2780(6)	0.2852(3)	0.2855(7)	4.0(2)
O4	0.1027(6)	0.2218(3)	0.3804(8)	4.2(2)
O5	0.1228(7)	0.3791(3)	0.3699(9)	5.1(2)
C1	0.1550(9)	0.2540(5)	0.724(1)	3.8(2)
C2	0.109(1)	0.2611(6)	0.860(1)	5.5(3)
C3	0.3731(9)	0.3342(5)	0.608(1)	4.0(2)
C4	0.436(1)	0.3806(6)	0.677(2)	6.5(4)
C5	0.2164(9)	0.4700(5)	0.377(1)	4.5(3)
C6	0.1227(9)	0.4344(5)	0.362(1)	3.5(2)
C7	0.0288(8)	0.4680(4)	0.3373(9)	3.0(2)
C8	−0.0598(9)	0.4367(5)	0.315(1)	3.9(2)
C9	−0.1442(9)	0.4688(6)	0.291(1)	4.8(3)
C10	0.657(2)	0.0300(9)	0.052(2)	9.6(6)*
C11	0.737(2)	0.061(1)	0.063(2)	10.0(6)*
C12	0.816(2)	0.050(1)	0.074(3)	6.6(7)*
C12′	0.855(2)	0.020(1)	0.074(3)	7.2(8)*

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

Table 3. Selected Bond Distances (Å) and Angles (°) Concerning Mo$_2$ Core for **3**·nC$_6$H$_6$ with Their Estimated Standard Deviations in Parentheses[a)]

Mo–Mo′	2.117(1)	Mo–O3	2.123(7)
Mo–O1	2.106(7)	Mo–O4	2.121(8)
Mo–O2	2.135(7)	Mo–O5	2.522(8)
O1–Mo–O2	86.2(3)	O2–Mo–O3	93.5(3)
O1–Mo–O3	176.4(3)	O2–Mo–O4	176.5(3)
O1–Mo–O4	92.7(3)	O3–Mo–O4	87.5(3)
Mo′–Mo–O5	169.0(2)	Mo–O5–C6	147.3(8)

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

ment of Mo$_2$(O$_2$CCF$_3$)$_4$ dimers and 1,4-nq molecules similarly to **1** and **2**. The crystallographic inversion centers are located at the midpoints of the Mo–Mo bonds. The oxygen atoms of 1,4-nq are coordinated to the dimer unit with a distance of 2.522(8) Å, which is comparable to those of **1** and **2** (2.478(6)—2.619(9) Å). The Mo–Mo bond length, 2.117(1) Å, is also comparable to those of **1** (2.107(1) Å) and **2** (2.108(1) and 2.111(1) Å). The average Mo–O(O$_2$CCF$_3$) distance is 2.121[17] Å,[14)] which is slightly longer than that of the parent Mo$_2$(O$_2$CCF$_3$)$_4$ dimer (2.06[12] Å).[10)] The Mo–O5–C6 bond angle (147.3(8)°) shows that **3**·nC$_6$H$_6$ has a zigzag chain structure. A zigzag chain of **2** consists of the Mo$_2$ dimer, the two axial positions of which are occupied by the carbonyl oxygens adjacent to the methyl groups of 2,6-dmbq and the dimer with less sterically hindered carbonyl oxygens of 2,6-dmbq at the axial positions (Fig. 1(b)). On the other hand, complex **1** has a step chain structure containing two kinds of 9,10-aq molecule, AQ1 (linking the Mo$_2$ dimers with the linear mode) and AQ2 (linking the Mo$_2$ dimers with the tilting mode) (Fig. 1(a)).

Table 4 lists structural parameters of the Mo$_2$ frameworks of **1**, **2**, and **3**·nC$_6$H$_6$ together with those of Mo$_2$(O$_2$CCF$_3$)$_4$.[10)] The Mo–Mo and Mo–O(O$_2$CCF$_3$) bonds are both slightly elongated in all the chain complexes. The carbonyl oxygens of the p-quinones are coordinated to the dimer cores with distances of 2.478(6)—2.619(9) Å, which are appreciably larger than those of the same type of chain complexes [Rh$_2$(O$_2$CCF$_3$)$_4$(p-quin)]$_n$ (p-quin = 1,4-benzoquinone, 1,4-nq, and 2,3-dimethyl-1,4-benzoquinone) 2.248(5) Å (p-quin = 1,4-benzoquinone), 2.248(3) Å (p-

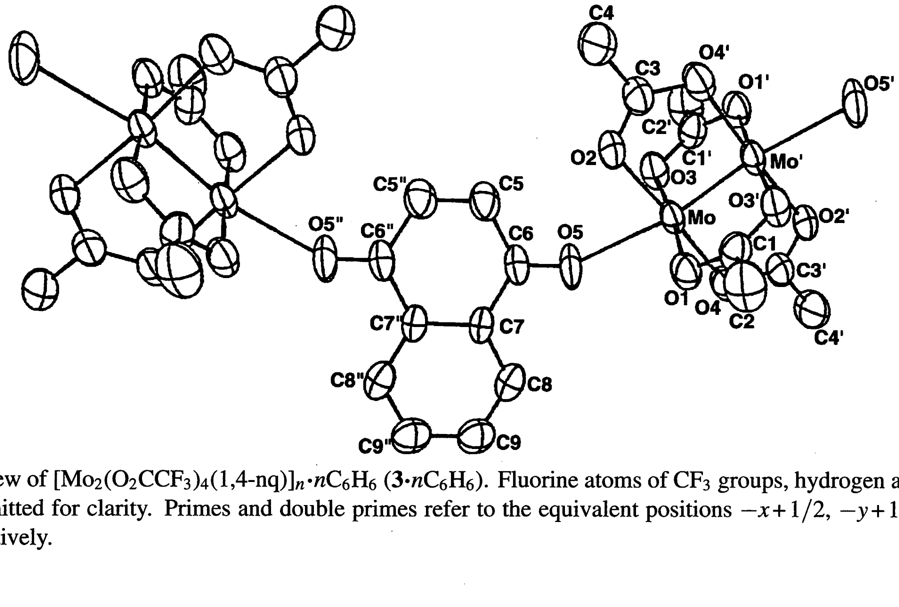


Fig. 2. ORTEP view of [Mo$_2$(O$_2$CCF$_3$)$_4$(1,4-nq)]$_n$·nC$_6$H$_6$ (**3**·nC$_6$H$_6$). Fluorine atoms of CF$_3$ groups, hydrogen atoms, and benzene molecules are omitted for clarity. Primes and double primes refer to the equivalent positions $-x+1/2$, $-y+1/2$, $-z+1$) and (x, $-y+1$, z), respectively.

Table 4. Structural Parameters Concerning $\mathrm{Mo_2}$ Frameworks of **1**, **2**, **3**$\cdot n\mathrm{C_6H_6}$, and $\mathrm{Mo_2(O_2CCF_3)_4}$

Complex	Mo–Mo/Å	Mo–O$_{\mathrm{eq}}$/Å	Mo–O$_{\mathrm{ax}}$/Å	Mo–O$_{\mathrm{ax}}$–C/°	Ref.
$\mathrm{Mo_2(O_2CCF_3)_4}$	2.090(4)	2.06[12][a]			10
1	2.107(1)	2.118[18][a]	2.478(6), 2.532(5)	178.7(7), 136.7(5)	This work
2	2.108(1), 2.111(1)	2.123[14][a]	2.619(9), 2.596(10)	152.6(7), 141.7(8)	This work
3$\cdot n\mathrm{C_6H_6}$	2.117(1)	2.121[17][a]	2.522(8)	147.3(8)	This work

a) Mean values.

quin = 1,4-nq), and 2.247(9) Å (*p*-quin = 2,3-dimethyl-1,4-benzoquinone).[6d] This is in accordance with the general tendency concerning the Mo–O$_{\mathrm{ax}}$ distance for the axially coordinated $\mathrm{Mo_2(O_2CR)_4}$ and $\mathrm{Rh_2(O_2CR)_4}$ complexes.[1]

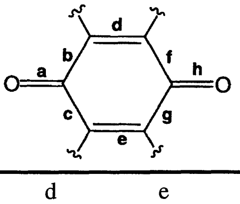
In Table 5, bond distances of *p*-quinone moieties for **1**, **2**, and **3**$\cdot n\mathrm{C_6H_6}$ are listed with the data for the free 9,10-aq, 2,6-dmbq, and 1,4-nq molecules.[15—17] It is clearly shown that considerable changes occur in the bond length values for the 2,6-dmbq molecule of **2**; the C=O double bonds are elongated by ca. 0.06 Å, the C=C double bonds by ca. 0.01 Å, and the C–C bonds connecting the carbonyl carbon and the olefinic carbon shortened by ca. 0.03 Å. In the case of **1**, such changes are observed for AQ2 although degree of the changes is much smaller than that of **2**. On the contrary, the 1,4-nq molecule of **3**$\cdot n\mathrm{C_6H_6}$ remains unaltered on the coordination.

The structural change of 2,6-dmbq of **2** is quite similar to that found for the reduction from DDQ to $[\mathrm{DDQ}]^{\bullet -}$ (DDQ = 2,3-dichloro-5,6-dicyanobenzoquinone).[18] In the reduced form, the C=O double bonds and the C=C double bonds are elongated by ca. 0.04 Å and by ca. 0.03 Å, respectively, but the C–C bonds connecting the carbonyl carbon and the olefinic carbon are shortened by ca. 0.02 Å (for the bonds adjacent to the CN group) or ca. 0.05 Å (for the bonds adjacent to the Cl group).[19] Reduction of the *p*-quinone does not seem to take place in the case of **2** because there is no significant change in the Mo–Mo bond[20] and it shows diamagnetic nature ($\mu_{\mathrm{eff}} = 0.70$ B.M. per $\mathrm{Mo_2}$ dimer (291 K)[21]). However, similarity in the structural change with that for $\mathrm{DDQ} \rightarrow [\mathrm{DDQ}]^{\bullet -}$ reduction might allow the interpretation that charge delocalization from the $\mathrm{Mo_2}$ core to the *p*-quinone moiety may occur to a certain degree. This interpretation would bring about a problem with the negligible structural change of the 1,4-nq molecule of **3**$\cdot n\mathrm{C_6H_6}$ in spite of its having the same oxidizing ability as 2,6-dmbq. Here, we offer a possible interpretation based on the molecular symmetry of the *p*-quinones. 2,6-Dmbq has a mirror plane through the carbonyl oxygens while 1,4-nq does not have it, which might be related to the difference between **2** and **3**$\cdot n\mathrm{C_6H_6}$. This explanation does not contradict the fact that AQ2 of **1** shows some structural deformation on the coordination in spite of the much weaker oxidizing ability than 1,4-nq (9,10-aq has the mirror plane along the C=O bonds).

Diffuse reflectance spectra of **1**—**3** and $\mathrm{Mo_2(O_2CCF_3)_4}$ are shown in Fig. 3. The δ—δ* transition band[22] observed at 430 nm for $\mathrm{Mo_2(O_2CCF_3)_4}$ is located around 440 nm as a peak or shoulder absorption for all the complexes. It is noted that the spectral features of **3** are apparently closer to those of $\mathrm{Mo_2(O_2CCF_3)_4}$ than those of **1** and **2**. On taking into account that the *p*-quinones show only weak n—π* transition bands[23] ($\lambda_{\mathrm{max}} = 405$ nm (for 9,10-aq; $\varepsilon = 89\ \mathrm{mol^{-1}\,dm^3\,cm^{-1}}$ in ethanol), 429 nm (for 2,6-dmbq; $\varepsilon = 28\ \mathrm{mol^{-1}\,dm^3\,cm^{-1}}$ in $\mathrm{CHCl_3}$), and 425 nm (for 1,4-nq; $\varepsilon = 32\ \mathrm{mol^{-1}\,dm^3\,cm^{-1}}$ in isooctane)) around 400 nm, the broadness of the peaks of **1** and **2** in this region may be due to appearance of a possible change transfer band from the $\mathrm{Mo_2}$ dimer to the *p*-quinone around there associated with the change delocalization between the $\mathrm{Mo_2}$ core and the *p*-quinone moiety; the δ—δ* transition band of **3** is more distinctive than those of **1** and **2**.

In this study, based on the structural comparison of the

Table 5. Bond Distances of the *p*-Quinone Moieties for **1**, **2**, and **3**$\cdot n\mathrm{C_6H_6}$ and Free 9,10-aq, 2,6-dmbq, and 1,4-nq (Å)



Complex		a	b	c	d	e	f	g	h	Ref.
1	AQ1	1.214(9)	1.481(9)	1.461(11)	1.394(10)	1.394(10)	1.461(11)	1.481(9)	1.214(9)	This work
	AQ2	1.229(8)	1.477(9)	1.444(11)	1.417(10)	1.417(10)	1.444(11)	1.477(9)	1.229(8)	
2		1.279(14)	1.45(2)	1.46(2)	1.35(2)	1.35(2)	1.44(2)	1.43(2)	1.28(2)	This work
3$\cdot n\mathrm{C_6H_6}$		1.214(12)	1.50(2)	1.49(2)	1.32(2)	1.399(13)	1.50(2)	1.49(2)	1.214(12)	This work
9,10-aq		1.213(11)	1.472(11)	1.495(11)	1.401(11)	1.401(11)	1.495(11)	1.472(11)	1.213(11)	15
2,6-dmbq		1.224(2)	1.483(2)	1.483(2)	1.336(2)	1.336(2)	1.459(2)	1.459(2)	1.229(2)	16
1,4-nq[a]		1.21	1.48	1.43	1.31	1.39	1.45	1.46	1.22	17

a) Estimated standard deviations (esd) for the bond lengths are not described in the literature.

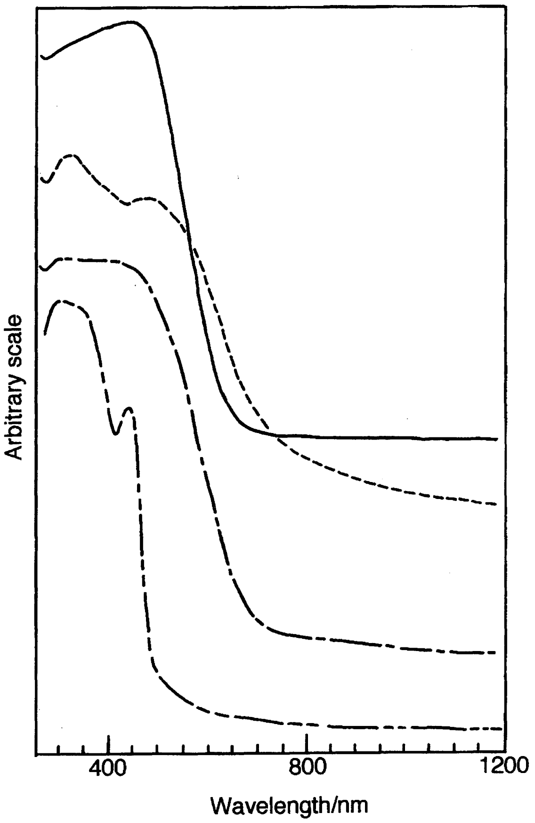


Fig. 3. Reflectance spectra of **1** (——), **2** (– – –), **3** (- - -), and $Mo_2(O_2CCF_3)_4$ (–··–).

chain complexes $[Mo_2(O_2CCF_3)_4(p\text{-quin})]_n$ (*p*-quin = 9,10-aq, 2,6-dmbq, and 1,4-nq), it has been proposed that charge delocalization from the Mo_2 dimer to the *p*-quinone possibly occurs in connection with the symmetry of the *p*-quinone. In order to verify this proposal, further study is in progress in our laboratories by changing the substituent groups on the *p*-quinone skeleton.

This work was partially supported by a Grant-in-Aid for Scientific Research No. 08404046 from the Ministry of Education, Science, Sports and Culture and by a grant from the Electric Technology Research Foundation of Chugoku.

References

1) F. A. Cotton and R. A. Walton, "Multiple Bonds between Metal Atoms," 2nd ed, Oxford Univ. Press, New York (1993).

2) F. A. Cotton, Y. Kim, and T. Ren, *Inorg. Chem.*, **31**, 2723 (1992); F. D. Cukiernik, A.-M. Giroud-Godquin, P. Maldivi, and J.-C. Marchon, *Inorg. Chim. Acta*, **215**, 203 (1994); J. L. Wesemann and M. H. Chisholm, *Inorg. Chem.*, **36**, 3258 (1997); M. C. Kerby, B. W. Eichhorn, J. A. Creighton, and K. P. C. Vollhardt, *Inorg. Chem.*, **29**, 1319 (1990); B. W. Eichhorn, M. C. Kerby, K. J. Ahmed, and J. C. Huffman, *Polyhedron*, **10**, 2573 (1991); E. F. Day, J. C. Huffman, K. Folting, and G. Christou, *J. Chem. Soc., Dalton Trans.*, **1997**, 2837; M. Handa, K. Kasamatsu, K. Kasuga, M. Mikuriya, and T. Fujii, *Chem. Lett.*, **1990**, 1753; M. Handa, K. Yamada, T. Nakao, K. Kasuga, M. Mikuriya, and T. Kotera, *Chem. Lett.*, **1993**, 1969; M. Handa, M. Mikuriya, R. Nukada, H. Matsumoto, and K. Kasuga, *Bull. Chem. Soc. Jpn.*, **67**, 3125 (1994); M. Handa, M. Mikuriya, T. Kotera, K. Yamada, T. Nakao, H. Matsumoto, and K. Kasuga, *Bull. Chem. Soc. Jpn.*, **68**, 2567 (1995).

3) T. R. Felthouse, T.-Y. Dong, D. N. Hendrickson, H.-S. Shieh, and M. R. Thompson, *J. Am. Chem. Soc.*, **108**, 8201 (1986); A. Cogne, A. Grand, P. Rey, and R. Subra, *J. Am. Chem. Soc.*, **111**, 3230 (1989); A. Cogne, E. Belorizky, J. Laugier, and P. Rey, *Inorg. Chem.*, **33**, 3364 (1994); M. Handa, Y. Sayama, M. Mikuriya, R. Nukada, I. Hiromitsu, and K. Kasuga, *Bull. Chem. Soc. Jpn.*, **68**, 1647 (1995); M. Handa, Y. Sayama, M. Mikuriya, R. Nukada, I. Hiromitsu, and K. Kasuga, *Chem. Lett.*, **1966**, 201; M. Handa, Y. Sayama, M. Mikuriya, R. Nukada, I. Hiromitsu, and K. Kasuga, *Bull. Chem. Soc. Jpn.*, **71**, 119 (1998).

4) F. A. Cotton and Y. Kim, *J. Am. Chem. Soc.*, **115**, 8511 (1993); F. A. Cotton, Y. Kim, and J. Lu, *Inorg. Chim. Acta*, **221**, 1 (1994); X. Ouyang, C. Campana, and K. R. Dunbar, *Inorg. Chem.*, **35**, 7188 (1996); C. Campana, K. R. Dunbar, and X. Ouyang, *J. Chem. Soc., Chem. Commun.*, **1996**, 2427; S. C. Huckett, C. A. Arrington, C. J. Burns, D. L. Clark, and B. I. Swanson, *Synth. Met.*, **41—43**, 2769 (1991); D. Li, S. C. Huckett, T. Frankcom, M. T. Paffett, J. D. Farr, M. E. Hawley, S. Gottesfeld, J. D. Thompson, C. J. Burns, and B. I. Swanson, *ACS Symp. Ser.*, **449**, 33 (1992); K. R. Dunbar, *J. Cluster Sci.*, **5**, 125 (1994); K. R. Dunbar and X. Ouyang, *Mol. Cryst. Liq. Cryst.*, **273**, 21 (1995).

5) J. P. Collman, J. T. McDevitt, C. R. Leidner, G. T. Yee, J. B. Torrance, and W. A. Little, *J. Am. Chem. Soc.*, **109**, 4606 (1987); M. Hanack and M. Lang, *Chemtracts-Inorg. Chem.*, **8**, 45 (1996).

6) a) M. Handa, H. Sono, K. Kasamatsu, K. Kasuga, M. Mikuriya, and S. Ikenoue, *Chem. Lett.*, **1992**, 453; b) M. Handa, A. Takata, T. Nakao, K. Kasuga, M. Mikuriya, and T. Kotera, *Chem. Lett.*, **1992**, 2085; c) M. Handa, H. Matsumoto, T. Namura, T. Nagaoka, K. Kasuga, M. Mikuriya, T. Kotera, and R. Nukada, *Chem. Lett.*, **1995**, 903; d) M. Handa, M. Mikuriya, Y. Sato, T. Kotera, R. Nukada, D. Yoshioka, and K. Kasuga, *Bull. Chem. Soc. Jpn.*, **69**, 3483 (1996); e) M. Handa, T. Nakao, M. Mikuriya, T. Kotera, R. Nukada, and K. Kasuga, *Inorg. Chem.*, **37**, 149 (1998).

7) L. Jeftic and G. Manning, *J. Electroanal. Chem.*, **26**, 195 (1970).

8) O. Ryba, J. Pilař, and J. Petránek, *Collect. Czech. Chem. Commun.*, **34**, 2581 (1969).

9) R. D. Rieke, W. E. Rich, and T. H. Ridgway, *Tetrahedron Lett.*, **1969**, 4381.

10) F. A. Cotton and J. G. Norman, Jr., *J. Coord. Chem.*, **1**, 161 (1971).

11) F. E. Mabbs and D. J. Machin, "Magnetism and Transition Metal Complexes," Chapman and Hall, London (1973).

12) Crystal data, details concerning the data collection, and the final discrepancy factors for **1** and **2** are included in the deposited data.

13) C. K. Fair, "MolEN Structure Determination System," Delft Instrument, Delft, The Netherlands (1990).

14) In the cases of the average bond lengths, the estimated deviation, which is given in square brackets, is calculated as [ ] = $[\sum_n \Delta_i^2/n(n-1)]^{1/2}$, in which Δ_i is the deviation of the *i*th of *n* values from the arithmetic mean of the set.

15) A. Prakash, *Acta Crystallogr.*, **22**, 439 (1967).

16) D. Rabinovich and G. M. J. Schmidt, *J. Chem. Soc. B*, **1967**, 127.

17) P. J. Gaultier and C. Hauw, *Acta Crystallogr.*, **18**, 179 (1965).

18) G. Zanotti, A. D. Pra, and R. Bozio, *Acta Crystallogr., Sect. B.*, **38B**, 1225 (1982).

19) This kind of structural change has been also found for *p*-chloranil: G. Zanotti and A. D. Pra, *Acta Crystallogr.*, *Sect. B.*, **36B**, 313 (1980).

20) It is well known that the oxidation of the molybdenum(II) dimer with the direct metal–metal bond leads to the considerable elongation of the Mo–Mo bond: F. A. Cotton, B. A. Frenz, E. Pedersen, and T. R. Webb, *Inorg. Chem.*, **14**, 391 (1975); T.-L. C. Hsu, I.-J. Chang, D. L. Ward, and D. G. Nocera, *Inorg. Chem.*, **33**, 2932 (1994).

21) $\mu_{\text{eff}}=0.63$ B.M for **1** (291 K); $\mu_{\text{eff}}=0.67$ B.M. for **3** (291 K).

22) W. C. Trogler and H. B. Gray, *Acc. Chem. Res.*, **11**, 232 (1978); D. S. Martin, R. A. Newman, and P. E. Fanwick, *Inorg. Chem.*, **18**, 2511 (1979); M. C. Manning, G. F. Holland, D. E. Ellis, and W. C. Trogler, *J. Phys. Chem.*, **87**, 3083 (1983).

23) S. Berger and A. Rieker, in "The Chemistry of the Quinonoid Compounds," ed by S. Patai, John Wiley and Sons, London, New York, Sydney, and Toronto (1974), pp. 163—229.