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Binuclear Metal Complexes. LI.$^{1)}$ Synthesis and Characterization of the Tetrachloro-*o*-benzoquinone Adducts of Binuclear Iron(II) Complexes with 2-(Salicylideneamino)phenol and Its Substituted Homologs

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Binuclear iron(III) complexes $Fe_2(R\text{-}R'\text{-sap})_2(tcoq)$ have been prepared by the oxidation of binuclear iron(II) complexes $Fe_2(R\text{-}R'\text{-sap})_2$ with tetrachloro-*o*-benzoquinone (TCOQ), where $H_2(R\text{-}R'\text{-sap})$ represents 2-(salicylideneamino)phenols with the substituent R on the salicylaldehyde ring and the R′ on the *o*-aminophenol ring. Magnetic measurements indicated the operation of an intramolecular antiferromagnetic spin-exchange interaction between the iron(III) ions, the exchange integrals being evaluated at -6—$-10\ cm^{-1}$. In both polarograms and cyclic voltammograms of these complexes, two redox processes attributable to Fe(III)–Fe(III) $\rightleftarrows$Fe(III)–Fe(II)$\rightleftarrows$Fe(II)–Fe(II) were observed.

Previously we showed that binuclear manganese(II) complexes $Mn_2(R\text{-}R'\text{-sap})_2$ of 2-(salicylideneamino)phenols ($H_2(R\text{-}R'\text{-sap})$; R and R′ being the substituents on the salicylaldehyde and the *o*-aminophenol rings, respectively) react with tetrachloro-*o*-benzoquinone (TCOQ) in an atmosphere of nitrogen to form binuclear manganese(III) complexes $Mn_2(R\text{-}R'\text{-sap})_2(tcoq)$, where two metal ions are bridged by the two phenolic oxygens of the Schiff bases in the equatorial plane and by the tetrachlorocatecholate group at the apical position (Fig. 1).$^{2)}$ These complexes are very sensitive to moisture, hence decompose into $Mn(R\text{-}R'\text{-sap})_2$ and $Mn_2(R\text{-}R'\text{-sap})_2$ in an open atmosphere.$^{2)}$

As an extension of the above investigation, in this study we have prepared the binuclear iron(III) complexes $Fe_2(R\text{-}R'\text{-sap})_2(tcoq)$ and examined their properties in terms of Mössbauer spectroscopy, polarography, cyclic voltammetry and cryomagnetic measurements, in comparison with $Mn_2(R\text{-}R'\text{-sap})_2(tcoq)$ and binuclear iron(III) complexes related to the present complexes.

Experimental

Preparations. 2-(Salicylideneamino)phenol and its homologs were obtained by the reaction of salicylaldehyde or a substituted salicylaldehyde with 2-aminophenol or a substituted 2-aminophenol in the 1:1 mole ratio. In this study, the following ligands were used (*cf.* Fig. 1); 2-(salicylideneamino)phenol ($H_2(sap)$), 2-(5-methylsalicylideneamino)phenol ($H_2(5\text{-Me-sap})$), 2-(salicylideneamino)-4-methylphenol ($H_2(4'\text{-Me-sap})$), and 2-(salicylideneamino)-4-chlorophenol ($H_2(4'\text{-Cl-sap})$).

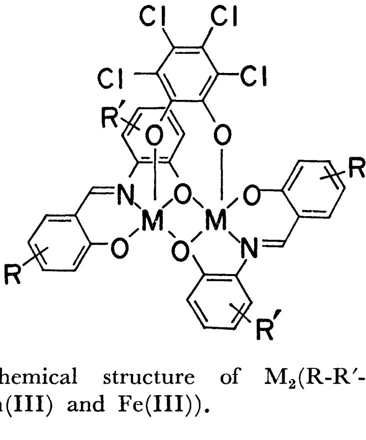

Fig. 1. Chemical structure of $M_2(R\text{-}R'\text{-sap})_2(tcoq)$ (M=Mn(III) and Fe(III)).

Binuclear iron(II) and iron(III) complexes, $Fe_2(R\text{-}R'\text{-sap})_2$ and $Fe_2(R\text{-}R'\text{-sap})_2X_2$ (X=Cl, Br), were prepared by the methods described in the literatures.$^{3,4)}$

$Fe_2(R\text{-}R'\text{-sap})_2(tcoq)$. Syntheses of the complexes were carried out in an atmosphere of nitrogen using a VAC Inert Atmosphere & Vacuum Deposition Equipment Model HE-43-2. The synthetic method for the complexes is exemplified by $Fe_2(sap)_2(tcoq)$. A mixture of $Fe_2(sap)_2$ (0.50 g) and TCOQ (0.23 g) in absolute acetonitrile (20 cm^3) was refluxed for 5 h and then stirred overnight at room temperature. Black crystalline powder separated was collected, washed with a small amount of acetonitrile and dried *in vacuo*.

Elemental analyses of the complexes are given in Table 1.

Measurements. Elemental analyses of carbon, hydrogen, and nitrogen were carried out at the Service Center of Elemental Analysis Kyushu University. Analyses of iron were made with a Shimadzu Atomic Absorption-Flame Spectrometer Model AA-610S. Infrared spectra were measured with a Hitachi Infrared Spectrometer Model 215 on KBr disks. Mössbauer spectra were measured by the constant acceleration method at room temperature, using a cobalt 57 source (5 mCi) diffused into palladium foil. The velocity of the spectrometer was calibrated by the use of a pure iron foil enriched with iron-57, which was also used as a reference for the isomer shift values. All the Mössbauer parameters were obtained by computer calculations. Magnetic susceptibilities were measured by the Faraday method in the temperature range from liquid nitrogen temperature to room temperature. The apparatus was calibrated by the use of $HgCo(NCS)_4$.$^{5)}$ Diamagnetic correction was made using Pascal's constants.$^{6)}$ Effective magnetic moments were calculated by the equation, $\mu_{eff}=2.828(\chi_A\times T)^{1/2}$, where χ_A is the susceptibility per one iron atom corrected for diamagnetism. Electronic spectra were recorded on a Shimadzu UV-VISIBLE Recording Spectrometer Model UV-240 and Shimadzu Multipurpose Spectrophotometer Model MPS-5000 in dichloromethane. Polarograms and cyclic voltammograms were recorded with a Yanagimoto Voltammetric Analyzer Model P-1000 in dichloromethane containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate as the supporting electrolyte. A three-electrode cell was used for measurements. The working electrode is a dropping mercury electrode for polarography and a glassy carbon for cyclic voltammetry. The auxiliary electrode and the reference electrode

Table 1. Elemental analyses of $Fe_2(R\text{-}R'\text{-}sap)_2(tcoq)$

	Found (%)				Calcd (%)			
	C	H	N	Fe	C	H	N	Fe
$Fe(sap)_2(tcoq)\cdot H_2O$	47.87	2.51	3.82	13.7	48.16	2.53	3.51	14.0
$Fe_2(5\text{-}Me\text{-}sap)_2(tcoq)\cdot 2H_2O$	48.60	2.73	3.28	13.0	48.38	3.10	3.32	13.2
$Fe_2(4'\text{-}Me\text{-}sap)_2(tcoq)\cdot H_2O$	49.75	2.94	3.52	13.3	49.44	2.92	3.39	13.5
$Fe_2(4'\text{-}Cl\text{-}sap)_2(tcoq)\cdot CH_3CN$	45.80	2.23	4.50	12.3	45.89	2.15	4.72	12.6

were a platinum coil and a saturated calomel electrode, respectively. All the potentials were corrected by the use of ferrocene as an internal standard (Fc^+/Fc: $E_{1/2}=0.40$ V *vs.* NHE).7)

Results and Discussion

Reaction of reddish brown $Fe_2(R\text{-}R'\text{-}sap)_2$ and TCOQ under nitrogen atmosphere yielded dark brown crystals. Elemental analyses suggested that these complexes contain $(R\text{-}R'\text{-}sap)^{2-}$, iron, and TCOQ in the ratio of 2:2:1. These complexes seem to be very stable in the open atmosphere, in contrast to the high sensitivity of $Mn_2(R\text{-}R'\text{-}sap)_2(tcoq)$ to moisture. Infrared spectrum of $Fe_2(sap)_2(tcoq)$ resembles that of $Mn_2(sap)_2(tcoq)$, suggesting the similarity in the structure between them. The reactions of $Fe_2(R\text{-}R'\text{-}sap)_2$ with 9,10-phenanthrenequinone or 1,2-naphthoquinone instead of TCOQ gave no pure adducts.

In order to clarify the oxidation state and the spin state of the iron in $Fe_2(R\text{-}R'\text{-}sap)_2(tcoq)$, the Mössbauer spectrum of $Fe_2(sap)_2(tcoq)$ was measured at room temperature and is shown in Fig. 2. The quadrupole splitting (ΔE_q) and the isomer shift (δ) of this complex were determined to be 1.05 and 0.44 mm s^{-1}, respectively. It is known that the isomer shifts for most high-spin five-coordinate iron(III) complexes fall in the range 0.35—0.48 mm s^{-1}.8,9) Thus, it is reasonable to assume that the iron in $Fe_2(R\text{-}R'\text{-}sap)_2(tcoq)$ is in a high-spin state and of five-coordination. This suggests that the complexes possess the binuclear structure with the bridging tetrachlorocatecholate group at the apical position (Fig. 1).

The line-area ratio of the quadrupole doublet is estimated at 1:1, but the line-widths of the doublet are not identical; the positive side band (0.512 mm s^{-1}) is a little larger than that of the other band (0.425 mm s^{-1}). Similar asymmetry in quadrupole doublet has been found for $[Fe(salen)Cl]_2$ ($salen^{2-}$=*N,N'*-disalicylideneethylenediamine dianion) at 78 K, while its quadrupole doublet becomes nearly symmetric at 4.2 K.4) According to Bergen *et al.* such asymmetry of Mössbauer doublet is attributable to the spin-spin relaxation.10,11) Asymmetric quadrupole doublet was also observed for $[Fe(salpa)Cl]_2$ ($salpa^{2-}$=2-salicylideneamino-1-propanol dianion) and other binuclear iron(III) complexes.9,12–14) In these complexes, spin-spin relaxation was regarded as the main reason for the asymmetric quadrupole splitting. Thus, it is likely that the asymmetric quadrupole doublet observed for $Fe_2(sap)_2(tcoq)$ is also due to the spin-spin relaxation, although Mössbauer spectra at low temperatures are not measured.

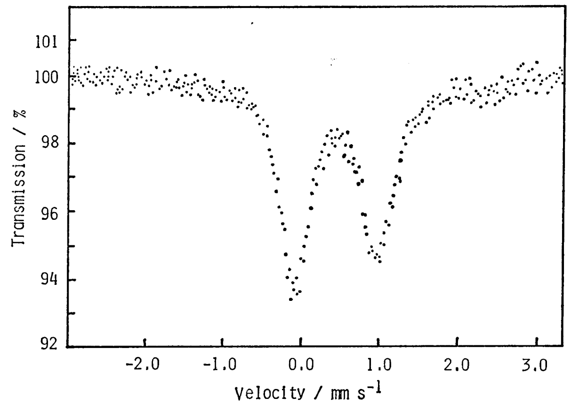

Fig. 2. Mössbauer spectrum of $Fe_2(sap)_2(tcoq)$.

Magnetic susceptibilities of $Fe_2(R\text{-}R'\text{-}sap)_2(tcoq)$ were measured in the temperature range 80—300 K. All of the complexes showed subnormal magnetic moments falling in the range 4.73—5.30 BM at room temperature (Table 2). Temperature-dependences of the magnetic moments suggested an operation of antiferromagnetic spin-exchange interaction between the metal ions. Based on the Heisenberg model ($\mathscr{H}=-2\Sigma J_{ij}S_iS_j$) and assuming no orbital contribution, the magnetic susceptibility equation for the Fe(III)-(S=5/2)-Fe(III)(S=5/2) system is given by

$$\chi_A=\frac{Ng^2\beta^2}{kT}\times\frac{55+30X^{10}+14X^{18}+5X^{24}+X^{28}}{11+9X^{10}+7X^{18}+5X^{24}+3X^{28}+X^{30}}+N\alpha$$
$$(X=\exp(-J/kT)),$$

where χ_A represents magnetic susceptibility per iron atom and other symbols have their conventional meanings. Magnetic susceptibilities of the present complexes could be well interpreted in terms of this equation. A typical example of best-fits of magnetic susceptibilities to the theoretical curve is shown in Fig. 3. Magnetic parameters ($-J$ and g) thus determined are given in Table 2 (temperature-independent paramagnetism $N\alpha$ being assumed at zero). The exchange integrals range from -6 cm^{-1} to -10 cm^{-1}.

These integrals are close to the values of other di-μ-alkoxo or di-μ-phenoxo bridged binuclear iron(III) complexes so far reported.4,15,16) It is particularly noticeable that the exchange integrals of the present complexes are essentially the same as those of $Fe_2(sap)_2X_2$ (X=Cl, Br).4) This fact implies that the antiferromagnetic spin-exchange interaction in $Fe_2(R\text{-}R'\text{-}sap)_2(tcoq)$ occurs *via* the phenolic oxygen bridge but not the tetrachlorocatecholate bridge.

Electronic spectra of the complexes $Fe_2(R\text{-}R'\text{-}sap)_2$-

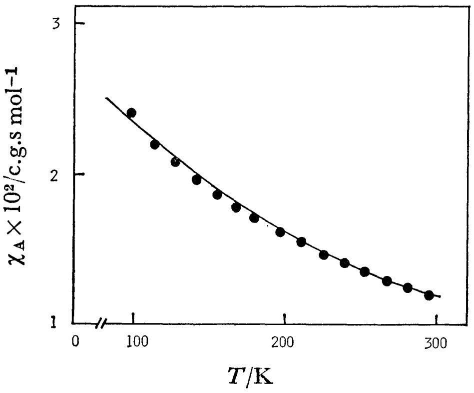

Fig. 3. Temperature variation of magnetic susceptibility for $Fe_2(sap)_2(tcoq)$. Solid curve is drawn based on the theoretical susceptibility equation using the parameters $g=1.98$, $-J=6.0\ cm^{-1}$ and $N\alpha=0$.

TABLE 2. EFFECTIVE MAGNETIC MOMENTS AT ROOM TEMPERATURE AND MAGNETIC PARAMETERS, J AND g, OF $Fe_2(R\text{-}R'\text{-}sap)_2(tcoq)$

	μ_{eff}/BM (T/K)	J/cm^{-1}	g
$Fe_2(sap)_2(tcoq)$	5.30(295.2)	−6	1.98
$Fe_2(5\text{-}Me\text{-}sap)_2(tcoq)$	4.75(296.6)	−10	2.00
$Fe_2(4'\text{-}Me\text{-}sap)_2(tcoq)$	5.00(296.1)	−8	2.00
$Fe_2(4'\text{-}Cl\text{-}sap)_2(tcoq)$	5.30(297.8)	−6	1.98

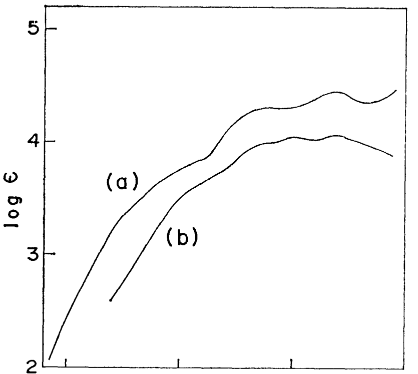

Fig. 4. Electronic spectra of (a)$Fe_2(sap)_2(tcoq)$ and (b) $Fe_2(sap)_2Cl_2$ in dichloromethane.

(tcoq) in dichloromethane are practically the same as each other, and were characterized by a strong absorption around $15\times10^3\ cm^{-1}$, which is absent in the spectrum of $Fe_2(sap)_2Cl_2$. The spectrum of $Fe_2(sap)_2(tcoq)$ is shown in Fig. 4. The spectrum of $Fe_2(sap)_2Cl_2$ is also shown for comparison. It is likely that the band at $15\times10^3\ cm^{-1}$ is due to the charge transfer band between iron(III) and tetrachlorocatecholate oxygen.

Electrochemical properties of the present complexes were investigated by means of polarography and cyclic voltammetry The complexes are stable in dichloromethane, judging from the fact that the electronic spectra obey Beer's law. Thus, electrochemical measurements were carried out in dichloromethane. All the complexes showed two quasi-reversible redox waves.

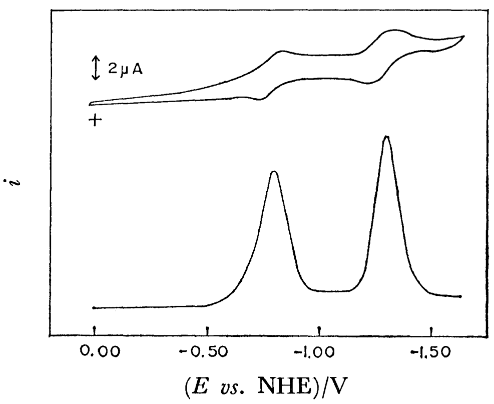

Fig. 5. Cyclic voltammogram (above) and differential pulse polarogram (below) of $Fe_2(5\text{-}Me\text{-}sap)_2(tcoq)$.

TABLE 3. REDOX POTENTIALS $E_{1/2}$ (V *vs.* NHE) OF $Fe_2(R\text{-}R'\text{-}sap)_2(tcoq)$

	DPP		CV	
	1st	2nd	1st	2nd
$Fe_2(sap)_2(tcoq)$	−0.77	−1.27	−0.91	−1.28
$Fe_2(5\text{-}Me\text{-}sap)_2(tcoq)$	−0.86	−1.36	−0.83	−1.32
$Fe_2(4'\text{-}Me\text{-}sap)_2(tcoq)$	−0.84	−1.34	−0.85	−1.35
$Fe_2(4'\text{-}Cl\text{-}sap)_2(tcoq)$	−0.90	−1.26	−0.91	−1.30

DPP: Differential pulse polarogram, CV: cyclic voltammogram.

Differential pulse polarogram and cyclic voltammogram of $Fe_2(5\text{-}Me\text{-}sap)_2(tcoq)$ are shown in Fig. 5. Half-wave potentials ($E_{1/2}$), which were determined from differential pulse polarogram and from the arithmetic mean of the cathodic and anodic peaks (E_{pc} and E_{pa}) of cyclic voltammogram, are given in Table 3.

Since binuclear zinc(II) complexes $Zn_2(R\text{-}R'\text{-}sap)_2$ do not show any redox process in the range 0——1.8 V, the redox processess observed for $Fe_2(R\text{-}R'\text{-}sap)_2(tcoq)$ can be attributed to those at the metal center. The first reduction occured at the potential −0.77——0.90 V and the second reduction at −1.26——1.36 V. The $\log(i/i_d-i)$ *vs.* E plots revealed that each process involves one-electron transfer. Based on these facts, we may tentatively attribute the first process to Fe(III)–Fe(III)$\rightleftharpoons$Fe(III)–Fe(II) and the second process to Fe(III)–Fe(II)$\rightleftharpoons$Fe(II)–Fe(II). It is to be noted that the redox potentials of $Fe_2(R\text{-}R'\text{-}sap)_2(tcoq)$ are practically independent of the substituents R and R′ on the ligand, while the redox potentials of $Mn(R\text{-}R'\text{-}sap)_2$[2] and $Zr(R\text{-}R'\text{-}sap)_2$[17] are reported to be markedly dependent on the substituents.

In order to compare the electrochemical property of $Fe_2(R\text{-}R'\text{-}sap)_2(tcoq)$ with that of $Fe_2(R\text{-}R'\text{-}sap)_2X_2$, cyclic voltammograms of $Fe_2(sap)_2Cl_2$ and $Fe_2(sap)_2Br_2$ were measured. The cyclic voltammograms, however, involved some complicated waves which could be hardly analyzed. It seems that $Fe_2(sap)_2X_2$ is partly dissociated or decomposed in solution.

Contrary to the step-wise redox behavior of $Fe_2(R\text{-}R'\text{-}sap)_2(tcoq)$, $Mn_2(sap)_2(tcoq)$ showed only one redox couple attributable to the process Mn(III)–Mn(III)$\rightleftharpoons$

Mn(II)–Mn(II).[2] The present complexes Fe_2(R-R′-sap)$_2$(tcoq) are insensitive to moisture, while the manganese(III) complexes Mn_2(R-R′-sap)$_2$(tcoq) are very sensitive to moisture. It seems that the difference in sensitivity to moisture between Fe_2(R-R′-sap)$_2$(tcoq) and Mn_2(R-R′-sap)$_2$(tcoq) is due to their different electrochemical properties.

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