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Syntheses and Properties of Binuclear Manganese(III) and Manganese(IV) Complexes with 1,2,3,4-Tetrakis(salicylideneamino)-2,3-diphenylbutane

Masaaki Nakamura,* Sayuri Shimokawa, Yuri Miyanaka, Hu Huang,† and Fumiaki Kai†
Department of Chemistry, Faculty of Science, Kumamoto University, Kumamoto 860
† Department of Environmental Science, Graduate School of Natural Science and Technology, Kumamoto University, Kumamoto 860

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Synopsis. A new dichlorodimanganese(III) and novel tetrachlorodimanganese(IV) complexes with 1,2,3,4-tetrakis(salicylideneamino)-2,3-diphenylbutane were prepared and characterized. The obtained dimanganese(IV) complex was rather stable to moisture in the solid state, but readily reduced to the corresponding dimanganese(III) complex in a methanol solution. The complexes can not be electrochemically formed as mixed valence states.

Binuclear manganese(III) and (IV) complexes have been receiving considerable attention as model systems for the photosynthetic oxygen-evolving complex.[1–4] From the viewpoint of these interests, many of the oxygen-bridged (μ-oxo, μ-hydroxo, and/or μ-phenyloxo) type binuclear manganese(III) and some μ-oxo type binuclear manganese(IV) complexes have been prepared and characterized.[5–9] In these complexes, the bridging oxo ligands are considered to play a role in connecting two or more high-valent manganese ions in the molecules. Actually, the binuclear manganese(IV) complexes reported hitherto regarding the above-mentioned interests are almost limited to the μ-oxo type complexes.[6–9]

In this paper we report on the syntheses and properties of a new type of binuclear manganese(III) and (IV) complexes with an octadentate Schiff base ligand, 1,2,3,4-tetrakis(salicylideneamino)-2,3-diphenylbutane (H_4sabzta), which do not contain a bridging oxo ligand. For the sake of a comparative study, the corresponding mononuclear manganese(III) and (IV) complexes with 1,2-bis(salicylideneamino)-1-phenylethane (H_2sabzen) were also prepared.

Experimental

Syntheses. The ligands, H_4sabzta and H_2sabzen, were prepared by a method described in our previous paper.[10]

[Mn_2(sabzta)Cl_2]: Manganese(II) chloride tetrahydrate (3.64 mmol) and tetrabutylammonium permanganate, (TBA)MnO_4, (0.78 mmol) were added to a dry ethanol solution (20 cm^3) containing H_4sabzta (2.21 mmol). This solution was refluxed for 2 h and then cooled to ambient temperature. The dark-brown crystalline powder obtained was collected. The crude product was recrystallized from methanol. The yield was ca. 42%. Found: C, 60.01; H, 4.24; N, 6.14%. Calcd for $C_{44}H_{34}N_4O_4Mn_2Cl_2 \cdot H_2O$: C, 59.95; H, 4.12; N, 6.36%.

[Mn(sabzen)Cl]: This complex was obtained as a dark-brown crystalline powder by reacting manganese(II) chloride tetrahydrate (1.79 mmol), (TBA)MnO_4 (0.60 mmol) and H_2sabzen (2.39 mmol) in dry ethanol (20 cm^3) in a way similar to the method for Mn_2(sabzta)Cl_2. The crude product was recrystallized from methanol. The yield was ca. 45%. Found: C, 59.42; H, 4.34; N, 6.02%. Calcd for $C_{22}H_{18}N_2O_2MnCl \cdot 3/4H_2O$: C, 59.21; H, 4.40; N, 6.28%.

[Mn_2(sabzta)Cl_4]: Mn_2(sabzta)Cl_2 (0.11 mmol) was suspended in dry acetone (20 cm^3); a methanol solution (2 cm^3) containing hydrochloric acid (0.21 mmol) was then added dropwise to the suspension. The obtained deep-green clear solution was filtered and the filtrate was concentrated under reduced pressure. The deep-green crystals obtained were collected and washed with dry acetone. The yield was ca. 23%. Found: C, 57.06; H, 4.22; N, 5.50%. Calcd for $C_{44}H_{34}N_4O_4Mn_2Cl_4 \cdot C_3H_6O$: C, 56.87; H, 4.06; N, 5.64%.

[Mn(sabzen)Cl_2]: This complex was obtained as deep-green crystals by treating Mn(sabzen)Cl (0.11 mmol) with hydrochloric acid in a way similar to that for Mn_2(sabzta)Cl_4. The yield was ca. 30%. Found: C, 56.25; H, 4.00; N, 5.77%. Calcd for $C_{22}H_{18}N_2O_2MnCl_2$: C, 56.43; H, 3.87; N, 5.98%.

Measurements. The IR spectra were recorded on a JASCO A-102 grating spectrometer on a KBr disk. Electronic spectra were recorded on a Hitachi 220A recording spectrophotometer. The electric conductivities were determined by a Horiba Conductivity Meter (Model DS-14). Polarograms were recorded on a Yanagimoto Polarographic Analyzer (Model P-1100) in dichloromethane containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate as the supporting electrolyte, by the use of a three-electrode cell equipped with glassy carbon as a working electrode, a platinum coil as an auxiliary electrode, and a saturated calomel electrode (SCE) as a reference electrode. In practice, all of the potentials were normalized by the use of ferrocene as an internal standard. The magnetic susceptibilities were measured by the Faraday method over the temperature range 85—300 K.

Results and Discussion

[Manganese(III) Complexes]. Since the binucleating ligand H_4sabzta has two "salen-like" donating sites, where H_2salen denotes 1,2-bis(salicylideneamino)ethane, the two manganese(III) ions in Mn_2(sabzta)Cl_2 are expected to hold in each of the above-mentioned donating sites. The IR spectrum of Mn_2(sabzta)Cl_2 is almost similar to that of the corresponding mononuclear complex Mn(sabzen)Cl and Mn(salen)Cl.[11] Further, it does not show any characteristic bands at 700—600 cm^{-1}, due to the presence of the μ-oxo or μ-peroxo structure.[6] The magnetic moments of Mn_2(sabzta)Cl_2 and Mn(sabzen)Cl per one manganese atom at room temperature are 5.08 and 4.90 BM, respectively. These obtained values are consistent with the spin-only value expected for a d^4 high-spin manganese(III) complex. The magnetic moment of the binuclear complex was almost independent of the temperature over the range 85—300 K, indicating the absence of a spin-exchange interaction between the metal ions. This is in contrast with the magnetic properties of the μ-oxo type dimanganese(III) complexes, in which a rather strong antiferromagnetic spin-exchange interaction between the manganese ions via oxo group(s) has been observed.[5–8]

Table 1. Electronic Spectral Data for Manganese(III) and (IV) Complexes

Complex	Solvent	$\tilde{\nu}/10^3\ \mathrm{cm}^{-1}$ ($\log\varepsilon$)			
$Mn_2(sabzta)Cl_2$	CH_2Cl_2	20.3 (3.24)	23.8 (3.67)	31.3 (4.21)	35.7 (4.33)
	CH_3OH		25.0 (3.79)		35.0 (4.33)
Mn(sabzen)Cl	CH_2Cl_2	20.8 (3.24)	23.8 (3.86)	31.7 (4.37)	35.7 (4.50)
	CH_3OH		25.3 (3.37)		35.5 (4.29)
$Mn_2(sabzta)Cl_4$	CH_2Cl_2	15.9 (3.61)	23.8 (3.83)	32.9 (4.32)	37.0 (4.56)
	CH_3OH		25.4 (3.67)		35.7 (4.19)
$Mn(sabzen)Cl_2$	CH_2Cl_2	15.9 (3.56)	23.8 (3.80)	33.0 (4.29)	37.2 (4.53)
	CH_3OH		24.9 (3.69)		35.6 (4.22)
$Mn(salen)Cl_2$[a)]	CH_2Cl_2	15.4 (3.60)	23.0 (3.78)		

a) Ref. 15.

The obtained complexes are soluble in both nondonor and donor solvents such as dichloromethane, chloroform, methanol, ethanol, and dimethylformamide. However, the electronic spectra of the complexes are sensitive to a kind of solvent; namely, different spectral features are observed in dichloromethane and in methanol (Table 1). These spectral properties resemble those of the pentacoordinated manganese(III) complexes with a "salen"-type ligand.[11-13] The molar conductivities of $Mn_2(sabzta)Cl_2$ and Mn(sabzen)Cl in methanol are 163 and 78 S cm^2 mol^{-1} at 25 °C, respectively, which are consistent with the expected values for 1:2 and 1:1 electrolytes, respectively.[14] These results strongly suggest that the chloride ions in the complexes are extensively dissociated and that solvated di- and monocationic complex ions, $[Mn_2(sabzta)]^{2+}$ and $[Mn(sabzen)]^+$, are formed in a methanol solution, respectively. It is concluded that the two manganese(III) sites do not interact intramolecularly, but act independently as the corresponding mononuclear complex.

[Manganese(IV) complexes]. In this study, a synthetic method for the mononuclear manganese(IV) complexes $Mn(salen)Cl_2$ and its homologues[15] was applied for the preparation of $Mn_2(sabzta)Cl_4$ and $Mn(sabzen)Cl_2$. The magnetic moments of these complexes are 3.90 and 3.80 BM per one manganese at room temperature, respectively; their values coincided well with the spin-only moment expected for the d^3 manganese(IV) ion. Matsushita et al. have reported that in manganese complexes with "salen"-type ligands a lower-frequency shift of ν(C–O) at the phenolate moiety was observed upon going from manganese(III) to (IV).[15] An analogous relationship exists in the present complexes; bands are observed at 1290 and 1300 cm^{-1} for the manganese(IV) and (III) complexes, respectively.

The manganese(IV) complexes obtained are soluble in dichloromethane, chloroform, and dry acetone; a deep-green solution is formed. The electronic spectra of these complexes in dichloromethane exhibit a new intense absorption band around 15900 cm^{-1} (Table 1), which is assignable to the CT transition from the Cl^- to the Mn(IV) ion on the basis of a resemblance to the reported spectra of $Mn(salen)Cl_2$ and its homologues.[15] From the magnetic and spectral properties of the binuclear manganese(IV) complex, it is concluded that the two manganese(IV) ions in this complex are also held in each of the two "salen-like" donating sites and have an octahedral geometry by coordinating two chloride ions at axial positions as well as the mononuclear complex, $Mn(sabzen)Cl_2$ and $Mn(salen)Cl_2$. As described above, it should be emphasized that this complex is the first example of a binuclear manganese(IV) complex lacking a bridging oxo ligand.

Table 2. Electrochemical Data for Manganese(III) and (IV) Complexes

Complex	E_{pc}	E_{pa}	ΔE_p	$E'_{1/2}$[a)]	$E_{1/2}$
	V	V	mV	V	V
$Mn_2(sabzta)Cl_2$	−0.690	−0.590	100	−0.640	−0.650 0.650
Mn(sabzen)Cl	−0.695	−0.595	100	−0.645	−0.655 0.615
$Mn_2(sabzta)Cl_4$	−0.710	−0.600	110	−0.655	−0.655 0.350
$Mn(sabzen)Cl_2$	−0.700	−0.590	110	−0.645	−0.645 0.360

a) $E'_{1/2}=(E_{pc}+E_{pa})/2$.

The methanolic solutions of manganese(IV) complexes do not show a deep-green color, but brown. Their electronic spectra are quite similar to those of the corresponding manganese(III) complexes in methanol (Table 1). The spectral difference of the manganese(IV) complex for dichloromethane and methanol solutions strongly indicates that the manganese(IV) complexes are reduced to the corresponding manganese(III) complexes. Unfortunately, it is ambiguous at present that the manganese(IV) complexes are reduced by either methanol or trace water contained in this solvent. Whereas $Mn_2(sabzta)Cl_4$ and $Mn(sabzen)Cl_2$ are rather stable to moisture in the solid state and show no appreciable changes in appearance, their IR spectra are observed when they are exposed to air for several months.

Both the present mononuclear and binuclear complexes exhibit redox waves at nearly the same potentials in dichloromethane (Table 2). Each of these four complexes exhibits only one reduction wave at around −0.65 V, which can be assigned to a quasi-reversible or irreversible one-electron reduction process for Mn(III) to Mn(II) on the basis of the peak separations (ΔE_p=100—110 mV) and their wave shapes in cyclic voltammograms.

However, their peak currents observed for the binuclear complexes are about twice, compared with the current of the corresponding redox waves for the mononuclear complexes, respectively. This electrochemical property is almost similar to that of the dicopper(II) complex with the same ligand, Cu_2(sabzta),[10] and can be interpreted in terms of the fact that binuclear complexes are electrochemically reduced by two simultaneous monoelectronic steps at nearly the same potential as that for the corresponding mononuclear complexes. In other words, the present binuclear manganese complexes can not be electrochemically formed as mixed valence states, such as Mn(III)-Mn(II).

The redox waves observed at the anodic region are also assigned to the irreversible one-electron redox process of Mn(III/IV), since the oxidation waves of the coordinated Schiff base ligands and chloride ion in these four complexes appeared at a more positive potential region. The reduction of Mn(IV) to Mn(III) for the manganese(IV) complexes occurs at about a 300 mV more cathodic region, compared with the corresponding oxidation potentials for the manganese(III) complexes. This shift of the redox potentials should indicate a stabilization of the manganese(IV) state by coordinating two chloride ions to metal centers.

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