Characterization of the Oxalato Complex of Manganese(IV)[1]

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The preparation and analysis of the oxalato complex of manganese(IV), referred to as $K_2[Mn(OH)_2(C_2O_4)_2]\cdot 2H_2O$ by Cartledge and Ericks, were reexamined. Measurements of magnetic moment confirmed the unusually low value, 2.48 B.M. at room temperature. The infrared spectra of the complex suggest the presence of oxide bridges between manganese atoms. The electrical conductance of aqueous solution of the complex salt at 0 °C has been measured in various concentrations. The results indicate that the complex anion is dimeric both in solid and in solution. The electronic spectra of the complex in powder and solution states were measured, and some decomposition processes discussed. It was proposed that the complex should be formulated as a dimer with two oxide bridges, $[Mn_2O_2(C_2O_4)_4]^{4-}$.

The preparation and properties of oxalato complex of quadrivalent manganese were first reported by Cartledge and Ericks.[2] Grey measured the magnetic moment of the complex and obtained the value 2.79 B.M. at room temperature.[3] This is much smaller than the spin-only value 3.87 B.M. for an ion of d^3 configuration. However, no detailed explanation has been given so far.

The present paper describes some physico-chemical measurements involving magnetic susceptibility, infrared and diffuse reflectance spectra of the solid complex as well as the electrical conductivity and electronic spectra of aqueous solutions. The results obtained are consistent with formulation of the complex anion as a dimer with two oxide bridges.

Experimental

Preparation of the Complex. The original method of preparation by Cartledge and Ericks[2] was followed with a slight modification. To 0.14 mol of oxalic acid dihydrate dissolved in 250 ml of redistilled water at 0 °C was added 0.04 mol of powdered potassium permanganate and 0.026 mol of patassium oxalate. Under vigorous agitation, the reaction began to take place at 7 °C evolving carbon dioxide, when the reaction mixture was cooled quickly to 0 °C. When the reaction was complete, the solution was filtered through a cold glass filter, the filtrate being collected in a beaker placed in a freezing mixture. To the filtrate was added 70 ml of cold ethanol in portions, the temperature being kept at 0 °C. The precipitated crystals were filtered off rapidly and washed successively with ice-cold 50% ethanol, 99% ethanol and absolute ether. The green crystals thus obtained were dried *in vacuo* over silica gel in a dark refrigerator (−5 °C). Although Cartledge and Ericks reported that under a microscope the solid was a mixture of green and golden yellow crystals, we obtained only green crystals in all runs. Found: K, 21.72; Mn, 15.17; $C_2O_4^{2-}$, 49.10%; Oxid. equiv., 181.2. Calcd for $K_4[Mn_2O_2(C_2O_4)_4]\cdot 4H_2O$: K, 21.65; Mn, 15.21; $C_2O_4^{2-}$, 48.74%; Oxid. equiv., 180.5.

Potassium trioxalatomanganate (III) was prepared by the method of Cartledge and Ericks.[4] Potassium dioxalatomanganate(II) was obtained by the reaction of manganese(II) oxalate and potassium oxalate.

Magnetic Measurements. Magnetic measurements were carried out at room temperature with the usual Gouy apparatus. Temperature dependence of the magnetic susceptibility was measured by the Fonor method[5] with an apparatus constructed at the Cryogenic Center of the University of Tokyo. Magnetic measurement of the aqueous solution of the complex was carried out by the method of Russel *et al.*[6]

Electrical Conductances. These were measured with a Yokogawa model BV-Z-103B conductivity bridge and platinized platinum electrodes. Sample solutions were prepared with CO_2-free water of 0 °C just before each measurement. The cell was thermostated at 0 °C. The temperature equilibrium was attained after 10 min. No significant decomposition took place during the course of measurements.

Spectral Measurements. The infrared spectra were measured by Nujol and hexachloro-1,3-butadiene mull methods with a model 403G infrared spectrophotometer (Japan Spectroscopic Co.). The electronic spectra of the complex in both solution and powder states were measured with Hitachi EPS-2 and 124 spectrophotometers. Temperature was controlled by circulating ice-water through a cell compartment. In order to remove cloudiness from the cell walls, a nitrogen gas stream was passed to the surface of the cell.

Potentiometric Titration. A Toa Electronics Ltd. model HM-5A pH meter with an HP-105 bright platinum electrode and an HC-907 calomel reference electrode was employed.

X-ray Measurements. The X-ray powder patterns were taken with a Rigaku Denki Geigerflex diffractometer using Ni-filtered Cu-*Kα* radiation. Relatively strong peaks were observed at lattice spacings *d*'s(A): 8.58, 7.96, 7.19, 3.63 and 3.30, indicating that the solid sample is crystalline.

Results and Discussion

Magnetic Properties. The magnetic susceptibility of the oxalato complex of manganese(IV) at room temperature increases with the elapse of time. This change is accompanied by the decrease in mass and increase in oxidation equivalent. Thus magnetic measurements were carried out as soon as the samples were prepared. Although somewhat higher values were obtained in earlier runs, repeated preparation and measurement of the susceptibility gave the magnetic moment, $\mu_{\text{eff}}=2.48$ B.M. (15.5—18.0 °C), which is definitely much below the spin-only value (*i.e.*, 3.87 B.M.).

The dried complex salt is soluble to some extent in water at room temperature but rapidly decomposes to give a colloidal solution. In the presence of oxalate ions, however, the complex is fairly stable in a cold solution. Thus the magnetic susceptibilities of the complex in oxalate solutions were measured at 3 °C. Results: 2.8 B.M. for 4.94×10^{-3} M solution and 2.7 B.M. for 15.05×10^{-3} M solution.

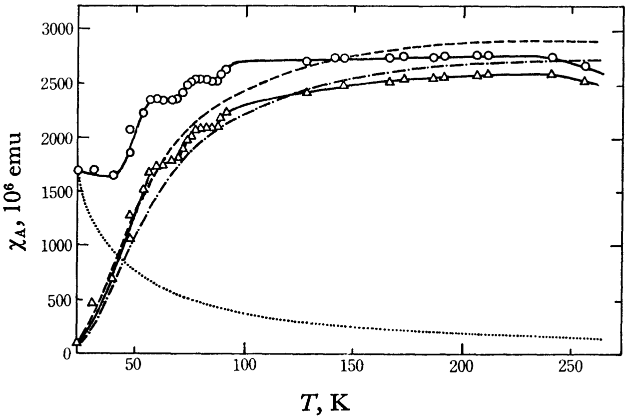


Fig. 1. Temperature dependence of magnetic susceptibility of the oxalato complex of manganese (IV).
—○—: experimental, —△—: experimental corrected for 1.9% Mn(III), ----; -·-·-: calculated for a binuclear cluster, $S_1=S_2=3/2$, $J=75$ "degrees" (----) and $J=80$ "degrees" (-·-·-), $g=2.00$ and $N\alpha=0$, ····: 1.9% Mn(III) with $\mu=3.87$ B.M.

In order to clarify the nature of the sub-normal moment, the temperature dependence of the susceptibility was examined in the range 300—23 K. The results are given in Fig. 1. It should be noted that the magnetic behavior of the complex deviates significantly from the Curie-Weiss law; the susceptibility remains nearly constant over the temperature range 240—90 K, but decreases abruptly and stepwise below 90 K. This suggests that there exists a large antiferromagnetic interaction between manganese atoms. Curves calculated by assuming binuclear cluster with $S_1=S_2=3/2$, $g=2.00$, $J=80$ or 75 "degrees" and $N\alpha=0$ are shown in Fig. 1.[7] They might account qualitatively for the temperature independent susceptibility in the higher temperature range, the deviation becoming significant in the lower temperature range. It was found during the course of study on the decomposition of the complex that the reaction is initiated by a trace of manganese(III) and proceeds autocatalytically. Thus, it was assumed that the complex contains some paramagnetic manganese(III) impurities formed during the course of measurement. The experimental values corrected for 1.9% of manganese(III) are plotted in Fig. 1. The curve so obtained fits fairly well the calculated one with $J=75$ "degrees" in the lower temperature range (below 60 K). However, the reason for the stepwise decrease in the susceptibility in the range 90—60 K is not clear.

Infrared Spectra. Main absorption peaks of the IR spectrum of the manganese(IV) oxalato complex are given in Table 1. For the sake of comparison, the IR data for both Mn(III) and Mn(II) oxalato complexes are also given. Tentative assignments of the bands are based on the works of Fujita *et al.*[8,9]

The bands at 3000—3600 cm^{-1} are much broader than expected for hydroxide ion in a complex.[10] They were assigned to the stretching vibrations of O–H of the water molecule.

Only the manganese(IV) complex gives two characteristic bands in the region 600—700 cm^{-1} (Fig. 2).

Table 1. Infrared spectra of oxalato complexes of manganese (cm^{-1})

$K_4[Mn_2O_2(ox)_4]\cdot 4H_2O$	$K_3[Mn(ox)_3]\cdot 3H_2O$	$K_2[Mn(ox)_2]\cdot 2H_2O$	Tentative assignments
3540(s) br	3550(s) br		ν(O–H) of H_2O
3450(s)	3440(s)	3430(s) br	
1712(s)	1711(sh)	1663(s)	
1673(s)	1682(s) br	1615(s) br	ν_{as}(C=O)
	1632(s)	1570(s)	
1377(s)	1378(s)	1453(s)	ν_s(C–O)
1230(s)	1256(s)	1315(s)	
895(m)	893(m)		
		855(m)	
812(m)	807(m)		
791(m)	788(m)	766(m)	
642(m) br			ν(Mn_2O_2)
618(m)			
	585(w)		
545(m)	522(m)br	494(w)	ν(Mn–O)
472(m)	485(m)	473(w)(sh)	
422(m)	396(m)	370(w)	ν(Mn–O)
338(m)			
306(w)br	282(w)br	256(m)	

s: strong, m: medium, w: weak, br: broad, sh: shoulder. ox: $C_2O_4^{2-}$.

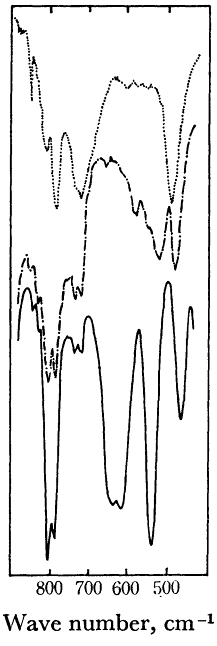


Fig. 2. IR spectra of oxalato complexes of manganese (in Nujol mulls).
——: $K_4[Mn_2O_2(C_2O_4)_4]\cdot 4H_2O$,
-----: $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$
····: $K_2[Mn(C_2O_4)_2]\cdot 2H_2O$

They might be assigned to the stretching modes of Mn_2O_2 bridges expected for binuclear complexes with two oxygen bridges.[11] It is noteworthy in this connection that the bands due to the bridging Mn–O bonds of poly, *catena*-oxo-*N*,*N'*-ethylenebis(salicylideneiminato)manganese(IV) appeared in the same region.[12]

The bond between manganese and oxygen of oxalato ligand (ν(Mn–O)) becomes stronger as the oxidation state of manganese atom increases. Fujita *et al.* pointed out that, in oxalato complexes of divalent metals, a shift of the M–O stretching band to a higher frequency is accompanied by a shift of the antisymmetric C–O stretching frequency to a higher frequency together with a shift of symmetric C–O stretching band to a lower frequency.[8,9] An analogous relationship exists in the three oxalato complexes of manganese of different oxidation states (Fig. 3).

Electrical Conductance. The electrical conductance of the complex in aqueous solution at 0 °C was measured in the concentration range 10^{-3}—10^{-2} equivalent/l. The equivalent conductance was plotted against the square root of the concentration (Fig. 4). For comparison, similar plots for salts of different valence types are also shown. The slope of the straight line for the oxalato complex resembles that for 4: 1 electrolyte rather than for the 2: 1 one.

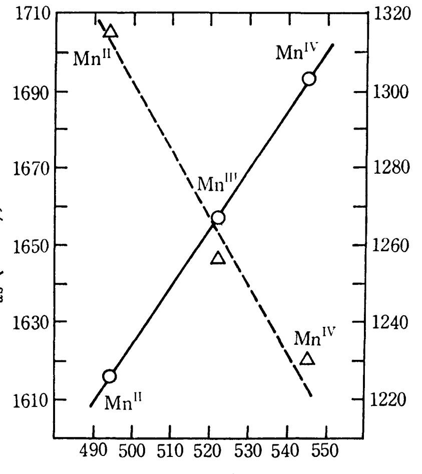


Fig. 3. Relationship between Mn–O stretching frequencies and C=O or C–O stretching frequencies of the oxalato complexes of manganese.
○: ν(C=O), △: ν(C–O).

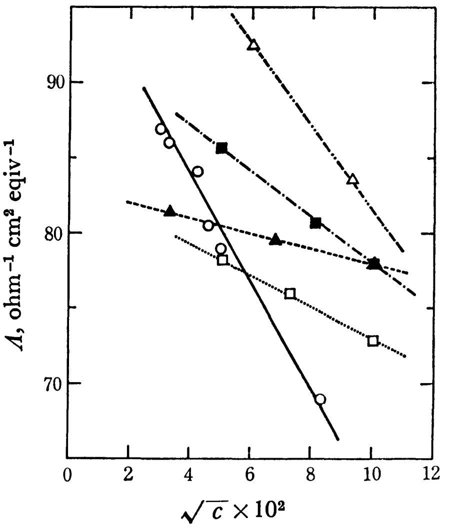


Fig. 4. Equivalent conductance (Λ, ohm^{-1} cm^2 equiv^{-1}) at 0 °C plotted against square root of concentrations (c, equiv/l) for the complex $K_4[Mn_2O_2(C_2O_4)_4]\cdot4H_2O$ and for typical 1: 1, 1: 2, 1: 3, and 1: 4 electrolytes.
○: $K_4[Mn_2O_2(C_2O_4)_4]\cdot4H_2O$, △: $K_4[Fe(CN)_6]$, ■: $K_3[Fe(CN)_6]$, □: K_2SO_4, ▲: KCl.

TABLE 2. ELECTRONIC SPECTRA OF THE OXALATO COMPLEX OF MANGANESE(IV) AND SOME OTHER COMPLEXES OF d^3 CONFIGURATION (cm^{-1})

$K_4[Mn_2O_2(C_2O_4)_4]\cdot4H_2O$	$[MnF_6]^{2-}$ b)	$[Cr(C_2O_4)_3]^{3-}$ b)	$[CrF_6]^{3-}$ b)	Transitions c)
26000(3.46) a)	21750	17500	14900	$^4A_{2g}\rightarrow{}^4T_{2g}(F)$
	28200	23900	22700	$^4A_{2g}\rightarrow{}^4T_{1g}$
			34400	$^4A_{2g}\rightarrow{}^4T_{2g}(P)$
13700(2.15) a) 15000(2.40) a)	16300	14300	15700 (16400)	$^4A_{2g}\rightarrow\begin{cases}^2T_{1g}\\ ^2E_g\end{cases}$
19600(2.34) a)			(22000)	$^4A_{2g}\rightarrow{}^2T_{2g}$
33600(3.96) a)				charge transfer
36000(3.99) a)				inner ligand

a) Values in parentheses relate to logarithms of molar extinction coefficients. b) cited from Ref. 13. c) tentative assignments for $K_4[Mn_2O_2(C_2O_4)_4]\cdot4H_2O$.

Electronic Spectra. Cartledge and Ericks reported on the visible absorption spectrum of the complex in oxalic acid solution.[2] We measured the spectra in a wider range involving the ultraviolet region in cold oxalate solutions. The absorption bands tentatively assigned, assuming d^3 configuration in an octahedral ligand field, are listed in Table 2 together with those of the mononuclear complexes of the iso-electronic configuration. As is predicted from the spectrochemical series, the 10Dq ($^4A_{2g}\rightarrow{}^4T_{2g}(F)$) of the oxalato complex of manganese(IV) is larger than that of $[MnF_6]^{2-}$ or $[Cr(C_2O_4)_3]^{3-}$.[13] The second d-d transition peak ($^4A_{2g}\rightarrow{}^4T_{1g}$) may be concealed by a broad charge transfer or inner ligand transition band. The intensities of the spin-forbidden transitions are considerably higher than expected. This might be due to metal-metal antiferromagnetic coupling.[14]

Figure 5 shows a diffuse reflectance spectrum of the solid complex (a) and a spectrum of the complex in a cold oxalate solution in the region 8000—22000 cm^{-1} ((b), Curve I). They are similar in shape and their peak positions are almost the same. We might say that no significant decomposition of the complex takes place in a cold oxalate solution.

When a sample solution containing oxalate was brought to room temperature, the deep green solution turned brown and later changed into pink forming trioxalatomanganate(III) ion. The latter eventually decomposed to give manganese(II) complexes. These changes are clearly seen in the spectral features shown in Fig. 5. As the absorption maximum at 15000 cm^{-1}

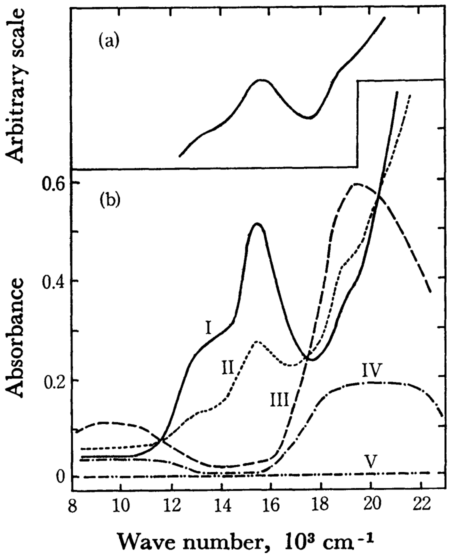


Fig. 5. Decomposition of the oxalato complex of manganese(IV) followed by spectral measurements.
(a) Diffuse reflectance spectrum of the solid complex.
(b) Time and temperature dependence of electronic spectra of the complex: 2.06×10^{-3} M in 0.1 M $Na_2C_2O_4$–$H_2C_2O_4$ solution (pH 4.9).
I: after 12 min, 4 °C, II: after 175 min, 5 °C,
III: after 222 min, 18 °C, IV: after 239 min, 18 °C,
V: after 12 hr, room temp.

decreases, the peak of trioxalatomanganate(III) at 19200 cm^{-1} increases in the initial stage. There appear three isosbestic points at 11800, 17300, and 20400 cm^{-1}. In connection with these changes, an attempt was made to follow the change in the magnetic susceptibility of manganese in 0.1 M oxalate solution (pH 4.9). Approximate values of the magnetic moment in 1.51×10^{-2} M (Mn) solution at 4—5 °C are as follows:

color	: green	brown	red	colorless
μ_{eff} (B.M.):	2.7	3.6	4.6	5.7

These results also confirm the view that the manganese(IV) complex is reduced finally to manganese(II) *via* manganese(III).

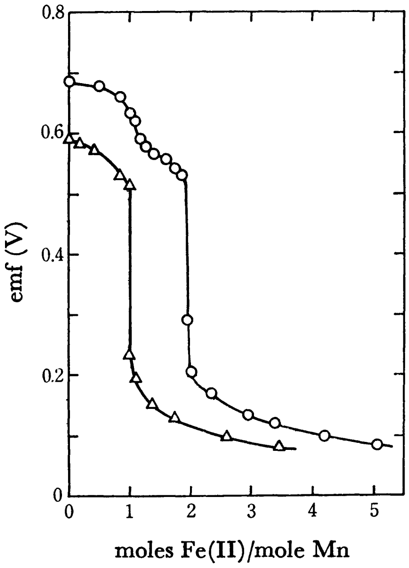
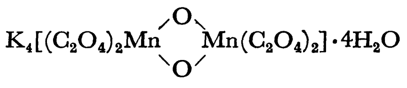


Fig. 6. Potentiometric titration of oxalato complexes of manganese (IV) and manganese (III) at 0 °C.
○: $K_4[Mn_2O_2(C_2O_4)_4]\cdot4H_2O$,
△: $K_3[Mn(C_2O_4)_3]\cdot3H_2O$.

Potentiometric Titration. A solution of the complex was titrated with iron(II) solution at low temperature. The result is illustrated in Fig. 6. For the sake of comparison, a titration curve of trioxalatomanganate(III) is also shown. The manganese(IV) complex gives two inflexion points corresponding to the steps, Mn(IV) to Mn(III) and Mn(III) to Mn(II). The standard redox potential, E° for a couple, Mn(IV)-oxalato complex/$[Mn(C_2O_4)_4]^{3-}$ was evaluated as *ca.* 0.95 V (NHE) at 0 °C. This value agrees with that calculated from the literature.[15]

Plausible Formula of the Complex. For the oxalato complex of manganese(IV), Cartledge and Ericks presented a formula $K_2[Mn(OH)_2(C_2O_4)_2]\cdot2H_2O$ on the basis of chemical analysis. However, it seems difficult to explain all the above-mentioned behavior of the complex with this formula.

Although the exact nature of the sub-normal magnetic moment has not been clarified yet, there is hardly any doubt that an exchange interaction between manganese atoms bridged by oxygen atoms exists in the complex anion. The electrical conductance behavior and infrared spectra support a dimeric structure. In this connection, di-μ-oxo structure of tetrakis(bipyridine)-dimanganese(III, IV) complex determined by X-ray diffraction could be compared.[16] Taking into account the above results, we propose as a plausible formula of the oxalato complex of manganese(IV) the following:



$$K_4[(C_2O_4)_2Mn\overset{O}{\underset{O}{\diamond}}Mn(C_2O_4)_2]\cdot4H_2O$$

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