maximum when this occurs, suggest the hypothesis that two of the oxalate ions are covalently bound, while the third is held by the weaker ionic forces. Such a structure would agree with the observed magnetic susceptibility. Further work is in progress in an attempt to gain more insight into the structure of these complexes.

Summary

1. The extinction coefficients of aqueous and buffered solutions of potassium trioxalatomanganiate and potassium dioxalatodiaquomanganiate at various concentrations have been measured in the visible region of the spectrum. The trioxalato salt has a maximum absorption at about 520 mμ and the dioxalato salt at about 450 mμ.

2. The two salts are convertible into each other according to the reaction

$$[Mn(C_2O_4)_3]^{=} + 2H_2O \rightleftharpoons [Mn(C_2O_4)_2(H_2O)_2]^{-} + C_2O_4^{=}$$

Equilibrium is established almost instantaneously. The equilibrium constant of the reaction has been determined by spectrophotometric analysis and found to be 3.8×10^{-3} at 0°.

3. The green and yellow dioxalato salts both give a golden-yellow solution with the same absorption curve, and the solution presumably consists of an equilibrium mixture of the two isomers. The optical evidence makes it likely that the yellow form is the statistically more probable *cis* isomer.

4. It is suggested that the complex manganiates may be derived from a covalent *dsp*^{2} structure fundamentally, the fifth and sixth valence bonds being ionic or ion-dipole in character.

BUFFALO, N. Y. RECEIVED JUNE 19, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF BUFFALO]

An Oxalato Complex of Quadrivalent Manganese

BY G. H. CARTLEDGE AND W. P. ERICKS

In the course of the investigation described in a previous paper[1] an attempt was made to prepare a hydroxo-oxalato complex compound containing tervalent manganese. In the previous experiments on the trioxalatomanganiate potassium permanganate was first reduced all the way to the manganous state by an excess of oxalic acid; the manganous ion was then oxidized by addition of a second portion of permanganate, the exact product being determined by the proportions of the reactants used. In view of the weakly acidic character of the water molecules in the dioxalatodiaquomanganiate ion, it was thought that the corresponding hydroxo ion might be obtained by suitable decrease of the hydrogen-ion concentration. Accordingly, a preparation was carried out in which part of the oxalic acid was replaced by potassium oxalate, using the proportions:

$$3.5H_2C_2O_4 : 0.5\ K_2C_2O_4 : KMnO_4$$

The materials were allowed to react at a little above 0° and the result was a mixture of two kinds of crystals. Microscopic examination showed the presence of some potassium trioxalatomanganiate along with a considerably larger proportion of dark, olive-green crystals. The experiment was repeated with further alteration in the reacting proportions until a method was finally developed which gave the green material in pure form. Although the substance is very unstable we were able to isolate it and prove that it contains quadrivalent manganese, its composition being represented accurately by the formula $K_2[Mn^{IV}(C_2O_4)_2(OH)_2]\cdot 2H_2O$. It is therefore to be called potassium dioxalatodihydroxomanganeate. So far as we have been able to discover it is the only known complex of quadrivalent manganese with the exception of the hexahalogenato complexes $[MnX_6]^{2-}$ and a diglycerol complex reported by Schottländer.[2]

Preparation.—The preparation is conducted according to the reaction

$$3.5H_2C_2O_4 + 0.65K_2C_2O_4 + KMnO_4 \longrightarrow K_2[Mn(C_2O_4)_2(OH)_2] + 0.5H_2C_2O_4 + 0.15K_2C_2O_4 + 3CO_2 + 2H_2O$$

The operations are conducted rapidly, in a cool and darkened room. Fourteen hundredths of a mole of oxalic acid (17.64 g. $H_2C_2O_4\cdot 2H_2O$) is dissolved in 250 cc. of distilled water. The solution is cooled to 0° and 0.04 mole (6.32 g.) of powdered potassium permanganate is added, followed by 0.026 mole of potassium oxalate (4.78 g. $K_2C_2O_4\cdot H_2O$). The mixture is agitated vigorously for about twenty minutes and the temperature is allowed to rise to 7°. At this point carbon dioxide begins to be

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[1] Cartledge and Ericks, THIS JOURNAL, **58**, 2061 (1936).

[2] Schottländer, *Ann.*, **155**, 230 (1870).

evolved rapidly, and the flask containing the mixture is submerged in an efficient cooling mixture to reduce the temperature quickly to 0°, the agitation being maintained meanwhile.

When the reaction is complete the solution has a dark green color. It is filtered rapidly through paper on a cold Büchner funnel, the filtrate being collected in a flask standing in a freezing mixture. Alcohol is added to the filtrate in small portions, keeping the temperature at about 0°, until 100 cc. has been added. The precipitation of the crystals begins almost at once.

The crystals are filtered rapidly and washed successively with ice-cold 50% alcohol, 95% alcohol, absolute alcohol and anhydrous ether. The filtrate from the crystals is red and upon standing often deposits the trioxalatomanganiate. The green crystals decompose rapidly at room temperature, especially in the light, but keep for some weeks if preserved in the dark at −6°.

Analysis.—The analytical procedures used were similar to those described in a preceding paper.[1] Volumetric and gravimetric determinations of manganese showed that two equivalents of iodine are liberated for each atomic weight of manganese, indicating the presence of quadrivalent manganese. In the determination of oxalate by titration with permanganate the proper allowance was made for the oxidation of a portion of the oxalate by the quadrivalent manganese. Before the final procedure had been developed as described above, five preparations were obtained which were somewhat impure but gave analyses with sufficient concordance to establish the composition. A sample prepared by the final procedure appeared to be homogeneous under the microscope and gave the following analysis:

Constituents	Found	Calculated for $K_2[Mn(C_2O_4)_2(OH)_2]\cdot 2H_2O$
K^+	20.3	20.62
Mn (gravimetric)	14.5	14.49
Mn^{4+} (volumetric)	14.3	
$C_2O_4^=$	46.2	46.42
H_2O (total)	14.2	14.26

Attempts to prepare the compound during the summer were at first unsuccessful, but the product was obtained without difficulty by the following method. The Büchner funnel was jacketed in an ice-bath, and closed at the top with a large one-holed rubber stopper. A glass tube passed from the funnel to the bottom of the reaction flask, which stood in a freezing mixture. The washing liquids were added through this flask by means of a separatory funnel; the air entering the flask and subsequently drawn through the crystals was first dried with calcium chloride and then chilled in a cooling coil. By this means the crystals were protected from the warm, humid air until completely washed and dried. Thorough and rapid drying is essential.

Although potassium dioxalatodihydroxomanganeate decomposes rapidly at room temperature, we have kept pure specimens for several weeks in a refrigerator at −6° before decomposition became apparent. The salt dissolves in water to give a clear, deep green, neutral solution which quickly becomes brown and turbid, and later changes into the red trioxalatomanganiate. The green color of a cold aqueous solution is unaffected by addition of small amounts of acids or alkalies. At 0° a solution containing a little oxalic acid remains clear and is stable enough to permit a determination of the absorption spectrum.

As obtained by the procedure described above, the product is an impalpable powder in which no distinct crystals can be seen under the microscope. The salt may be recrystallized as follows. The powder is dissolved in twenty-five times its weight of cold 0.1 *M* oxalic acid. After rapid filtration the solution, at 0°, is treated with one-sixth its volume of ice-cold 95% alcohol and placed in a freezing mixture until crystallization occurs. If the precipitation is sufficiently gradual well-defined crystalline rods are formed. A photomicrograph of one of our products is shown in Fig. 1; for this we are indebted to Professor E. Raymond Riegel. The crystals photographed were clearly seen to be of two colors, green and orange. Careful analysis showed the material to be pure, however, and it is probable that the two kinds of crystals were the *cis* and *trans* isomers theoretically possible. So far we have been unable to separate the two forms, owing to their instability.

Barium Dioxalatodihydroxomanganeate.—From the fact that our analysis indicated that we had a complex bivalent anion of rather large size, it was expected that its barium and lead salts should be sparingly soluble. Preliminary qualitative tests showed the correctness of this surmise, and the barium salt was obtained without difficulty. To 20 cc. of 5% barium chloride solution 1 cc. of concentrated hydrochloric acid was added. This mixture gives no precipitate of barium oxalate if a small quantity of oxalate ion is added. To 0.8 g. of potassium dioxalatodihydroxomanganeate dissolved in 40 cc. of ice-cold water, 13 cc. of the acidified barium chloride was added (a 25% excess). A silky precipitate appeared almost at once. The brown mixture was filtered, leaving a pale, apple-green precipitate which was washed and dried in the usual manner. The salt is sparingly soluble in water, giving a pale green color. Addition of sulfuric acid causes the color to disappear with the precipitation of barium sulfate. Analysis of the salt gave the following results:

Constituents	Found	Calculated for $Ba[Mn(C_2O_4)_2(OH)_2]\cdot 3H_2O$
Ba^{++}	29.8	30.09
Mn (gravimetric)	12.1	12.03
$C_2O_4^=$	38.6	38.56

Chloropentamminecobalti - dioxalatodihydroxomanganeate.—In qualitative tests it was found possible also to isolate the new complex ion as a sparingly soluble double complex with cobalt cations. Stoichiometrically equivalent amounts of chloropentamminecobalti chloride and potassium dioxalatodihydroxomanganeate were mixed, using 0.001 mole of each dissolved separately in the least possible quantity of water at 0°. Soon after mixing the solutions fine crystals formed, of fawn color with a greenish cast. The crystals were filtered rapidly and washed with cold alcohol and ether in the usual manner. The yield was 85%.

Microscopic examination showed that the product was homogeneous and had a needle-like structure. The crystals are sparingly soluble in water, forming a silky suspension. Upon addition of potassium oxalate the crystals gradually dissolve, giving a yellowish-green color. Sulfuric acid gives a brown solution which quickly changes to the pink of the chloropentamminecobalti ion. Qualitative tests showed the presence of cobalt and manganese. The double complex appears to be decidedly more stable than the potassium salt.

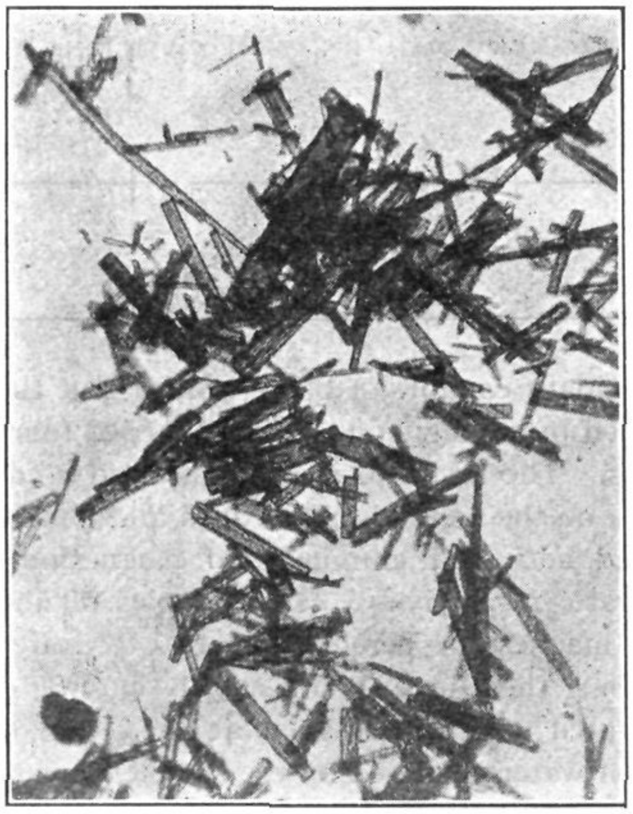

Fig. 1.—Potassium dioxalatodihydroxomanganeate, × 354.

The Absorption Spectrum of Potassium Dioxalatodihydroxomanganeate.—The absorption spectrum cannot be measured accurately in simple aqueous solution owing to the rapid appearance of a turbidity. In the presence of dilute oxalic acid, however, the solution remains clear and spectrophotometric measurements can be made with a considerable degree of accuracy, provided the solution is kept at 0° and the observations do not extend over three or four minutes on any one solution. Three series of determinations were made in 0.1 *M* oxalic acid, the concentration of the complex compound being 0.005, 0.01 and 0.025 *M*, respectively. The measurements were made with a Bausch and Lomb spectrophotometer, the precautions described in the preceding paper[3] being observed. The solutions were in all cases prepared immediately before use, and the cell was jacketed in ice during the measurements. The extinction coefficients obtained indicate that Beer's law is followed within the accuracy of the procedure over the concentration range employed. The solution has a minimum absorption at 566 mμ, with a pronounced maximum at 643 mμ, as shown in Fig. 2.

According to Pauling's theory of the bonds in complex compounds[4] quadrivalent manganese should be expected to form six equivalent octahedral bonds, since in its lowest state six d^2sp^3 eigenfunctions are available for bond formation. Magnetic susceptibility measurements cannot distinguish such a covalent structure from one involving purely ionic bonds in the present case, since both structures should give a susceptibility corresponding to three unpaired electrons. Considering the high valence of the manganese, however, it is more than likely that the covalent structure is favored.

It is noteworthy that in the case of tervalent manganese a diaquo complex forms readily and functions only very weakly as an acid, whereas with quadrivalent manganese the hypothetical aquo-ion dissociates into its corresponding hydroxo ion even in moderately acid solutions. This behavior is in accordance with the relation between the acidic strength of aquo ions and ionic potentials as developed by one of the authors.[5] From the ionic potential of quadrivalent manganese we should expect manganese dioxide to be somewhat more acidic than titanium dioxide. Although a sufficiently high hydrogen-ion concentration should theoretically convert the hydroxo ion into the aquo ion, there is no evidence from color changes that such an effect occurs in the presence of dilute acids. Higher hydrogen-ion concentrations cannot be used because of the rapid reduction of the manganese in strongly acid solutions. It is significant that Tschugajeff[6] has prepared a hydroxo complex of quad-

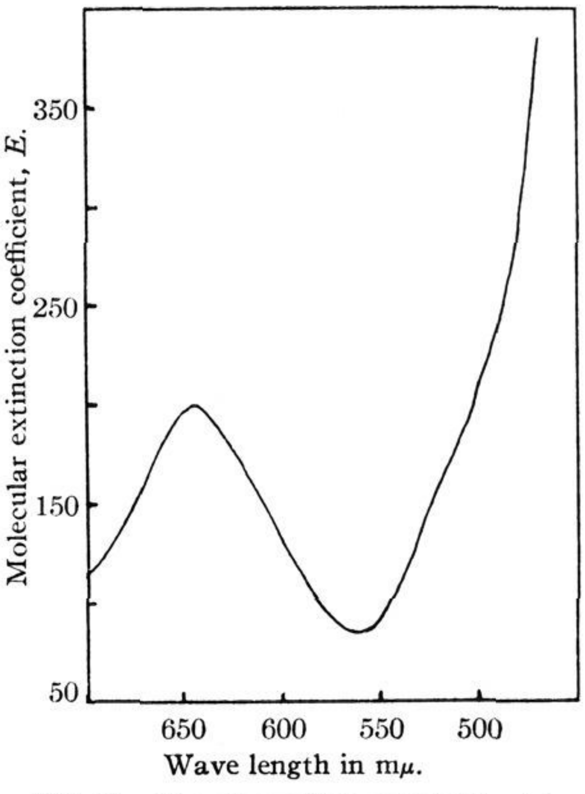

Fig. 2.—The absorption spectrum of potassium dioxalatodihydroxomanganeate in 0.1 *M* oxalic acid.

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(3) Cartledge and Ericks, THIS JOURNAL, **58**, 2065 (1936).

(4) Pauling, *ibid.*, **53**, 1367 (1931).

(5) Cartledge, *ibid.*, **50**, 2855, 2863 (1928).

(6) Tschugajeff, *Z. anorg. allgem. Chem.*, **137**, 1 (1924).

rivalent platinum which is not converted into an aquo compound even by concentrated hydrochloric acid.

Summary

1. A new complex compound of quadrivalent manganese has been prepared which has the composition $K_2[Mn(C_2O_4)_2(OH)_2]\cdot 2H_2O$. The barium and chloropentamminecobalti salts were also isolated.

2. The absorption spectrum was measured in the visible region.

BUFFALO, NEW YORK RECEIVED JUNE 19, 1936

NOTES

Sodium Fluorenone as a Dehydrating Agent[1]

BY H. E. BENT AND H. M. IRWIN, JR.

The most rapid method of drying an organic liquid is to dissolve in it some compound which reacts rapidly with water. For this purpose sodium benzophenone has been widely used although this involves using an alkali metal, sodium–potassium alloy or some other material which introduces considerable hazard into such work. Fluorenone has the advantage over benzophenone that it will react readily with dilute sodium amalgam to form an addition compound which has a deep green color and therefore like benzophenone gives a definite indication by its color of the absence of water. Dry solvent is then obtained by distilling from this solution.

The object of this investigation is to compare the efficiency of sodium fluorenone with the customary drying agents, magnesium perchlorate and activated alumina. Since the compound formed by the addition of sodium to fluorenone is more stable than that formed with benzophenone, it is important to be sure that the ketyl is still sufficiently reactive to be an effective drying agent.

A dilute solution of sodium fluorenone was prepared for this work by introducing 0.025 g. of fluorenone and evacuating with a mercury pump for one hour. Three to five cubic centimeters of a saturated amalgam (about 1%) was then added *in vacuo* and 50 cc. of dry ether. Shaking produced a solution which was sufficiently concentrated to react with at least one hundred times as much water as is retained by the glass on its surface.[2] A tube, connected to the reaction flask by a capillary capable of being broken and thereby opened by a magnetic hammer, carried four side-tubes. The first two were empty and used as a check on the method. The third and fourth contained activated alumina and magnesium perchlorate, respectively. The samples of alumina and magnesium perchlorate were prepared by exposing them in a thermostat to one liter of air saturated with water vapor at 25°. The quantity of water absorbed by the sample was at least one hundred times as much as was necessary to destroy the sodium fluorenone with which it came in contact, while still being small enough to give the very low vapor pressure characteristic of the dehydrating agent. The tubes containing the solid dehydrating agents were evacuated for a short time before sealing the apparatus, and immediately the capillary was broken in order to prevent diffusion from one solid to the other. The fluorenone was decolorized in the first empty tube on account of moisture on the glass and in the vapor state. In the second tube the solution retained its color. In the third and fourth tubes the solution was immediately decolorized by the alumina and by the magnesium perchlorate, indicating that the vapor pressure of water was sufficiently high to be removed by the ether solution of sodium fluorenone. A duplicate run verified the conclusion from this experiment.

The vapor pressure of water is given as 0.003 mm. for alumina and the water is given as unweighable in 210 liters for magnesium perchlorate.[3] If unweighable means less than 1 mg. this would give a vapor pressure of less than 0.005 mm. If we assume that in the presence of a small amount of water the ketyl is converted to fluorenone and fluorenole,[4] then we can estimate a mini-

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(1) This problem was studied as a reading period assignment in the first course in physical chemistry at Harvard University.

(2) Bent and Lesnick, THIS JOURNAL, **57**, 1246 (1935).

(3) Yoe, *Chem. News*, **130**, 340 (1935).

(4) Bachman, THIS JOURNAL, **55**, 1179 (1933).