2. A series of acid-soluble barbituric acids was prepared in which the N-aryl groups were *p*-dimethylaminophenyl and *p*-diethylaminophenyl. The 5,5-dialkyl groups were diethyl, ethyl-*n*-butyl, ethyl-isobutyl and ethyl-isoamyl.

TUCKAHOE, NEW YORK RECEIVED JULY 30, 1936

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

Oxalato Complex Compounds of Tervalent Manganese

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

Complex compounds containing manganese in the tervalent or quadrivalent state have been prepared in a few instances, but there has never been a thoroughgoing study of the field, such as has been made in the compounds of chromium and cobalt. From a consideration of the structure of the manganese atom there is every reason to expect it to form complexes readily, since the manganic ion has the combination of available *d*, *s* and *p* eigenfunctions which is required for the formation of covalent bonds, according to the theory of Pauling.[1] That so few of such possible compounds have been prepared is readily ascribed to the complicated oxidation–reduction relations of manganese. The simple manganic ion is like the cobaltic ion in its large oxidation potential, but is even more difficult to manipulate because of the readiness with which it dismutates into the manganous ion and manganese dioxide.

The oxalato complexes are of particular interest in connection with the kinetics of the reaction between potassium permanganate and oxalates.[2] Potassium trioxalatomanganiate, $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$, seems to have been prepared first by Souchay and Lenson.[3] Kehrmann[4] rediscovered the compound and isolated it in crystalline form. Meyer and Schramm[5] in 1922 attempted to prepare dioxalatodiaquomanganiates, but without success. Instead, they were able to obtain the corresponding dimalonatodiaquamanganiate, which is a fairly stable compound and readily prepared. In 1926 the same authors[6] reported that by treating cold sodium tetroxalate (in excess) with manganese dioxide they obtained an impure green material. This product was very unstable, turned yellowish-brown, and decomposed before it could be isolated for analysis. Meyer and Schramm concluded from analogy with the green sodium dimalonatodiaquomanganiate that the unstable product was the corresponding oxalato complex.

We have been able to prepare a number of pure compounds containing the trioxalatomanganiate and dioxalatodiaquomanganiate ions, as well as a difluodioxalato compound and, unexpectedly, a dioxalatodihydroxo complex of quadrivalent manganese. The oxalatomanganiates have turned out to be extremely interesting in that in aqueous solution they are easily converted one into the other, according to the reversible reaction

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

Using a spectrophotometric procedure we have been able to measure the equilibrium constant for this reaction, as will be shown in the following paper. The complexes are far more reactive than the corresponding chromium or cobalt compounds, but when properly isolated in pure form may be analyzed accurately and, in some instances, may be preserved indefinitely in a refrigerator.

Potassium Trioxalatomanganiate.—Our interest in the oxalato complexes arose from a need for some potassium trioxalatomanganiate of extreme purity, with particular reference to its freedom from iron. Trioxalato complexes are formed by tervalent chromium, iron and cobalt; the salts are all probably isomorphous with the manganic complex, and all of them have moderately high solubilities. Because of the instability of the manganic complex the principal purification is necessarily applied to the reagents rather than to the final product. We have accordingly devised a procedure which involves as few reagents as possible. The chief difficulty in obtaining a homogeneous product is due to the sparing solu-

---

(1) Pauling, THIS JOURNAL, **53**, 1367 (1931).

(2) Schilow, *Ber.*, **36**, 2735 (1903); Skrabal, *Z. anorg. Chem.*, **42**, 73 (1904); Schröder, *Z. öffentl. Chem.*, **16**, 270 (1910); Kolthoff, *Z. anal. Chem.*, **64**, 185 (1924); Deiss, *Z. angew. Chem.*, **39**, 664 (1926); Launer, THIS JOURNAL, **55**, 865 (1933); Launer and Yost, *ibid.*, **56**, 2571 (1934); Fessenden and Redmon, *ibid.*, **57**, 2246 (1935).

(3) Souchay and Lenson, *Ann.*, **105**, 254 (1858).

(4) Kehrmann, *Ber.*, **20**, 1594 (1887).

(5) Meyer and Schramm, *Z. anorg. Chem.*, **123**, 56 (1922).

(6) Meyer and Schramm, *ibid.*, **157**, 196 (1926).

bility of the acid oxalates, and numerous procedures were investigated before a dependable one was obtained.

The method which has been developed consists in reducing potassium permanganate with oxalic acid in proper excess, followed by oxidation of the resulting manganous oxalate by a second portion of permanganate which is added along with sufficient potassium carbonate to furnish the necessary potassium and the most favorable hydrogen-ion concentration. The over-all reaction and the stoichiometric proportions actually used are expressed by the equation

$$5H_2C_2O_4 + KMnO_4 + K_2CO_3 \longrightarrow K_3[Mn(C_2O_4)_3] + 5H_2O + 5CO_2 \quad (1)$$

Preparation of Reagents.—Water was prepared by redistilling the laboratory distilled water with alkaline permanganate, using a spray trap and condenser of block tin. The middle portion of this distillate was again redistilled in an all-quartz still for conductivity water.

Oxalic acid was prepared by the hydrolysis of ethyl oxalate, Eastman ester being used in part, along with a sample prepared in this Laboratory.[7] The hydrolysis of the redistilled ester (boiling range 1°), evaporation of the alcohol and recrystallization of the resulting oxalic acid were conducted entirely in quartz.

Potassium permanganate (Baker C. P.) was dissolved in warm purified water and after digestion filtered through acid-washed asbestos. The crystals obtained by evaporation and cooling were recrystallized in quartz four times.

Potassium carbonate was prepared from potassium acid tartrate obtained from pure tartaric acid and potassium carbonate. After four recrystallizations the acid salt was decomposed at as low a temperature as possible and the carbonate formed was evaporated to crystallization in a silver dish.

Alcohol and ether were purified and dehydrated in the usual manner. Before distillation the ether was agitated with potassium hydroxide and potassium permanganate. The quartz still was used for the distillations.

Preparation of Potassium Trioxalatomanganiate.—The stoichiometric proportions represented in equation (1) were used in the reaction, which, however, was conducted in two stages. To the entire quantity of oxalic acid to be used, four-fifths of the indicated amount of potassium permanganate was added and completely reduced. After the solution had cooled to about 0° the potassium carbonate and remaining potassium permanganate were added. All operations were carried out in quartz apparatus and in a darkened room. The details were as follows.

A quarter of a mole (31.5 g.) of oxalic acid dihydrate was dissolved in 200 cc. of pure distilled water in a 500-cc. beaker. The solution was heated to 70–75° and 0.04 mole (6.32 g.) of powdered potassium permanganate was added in small portions, while agitating the solution. When the solution had become colorless, 0.05 mole (6.9 g.) of solid potassium carbonate was added in small portions, with agitation. Occasional agitation was maintained to prevent the precipitate from sticking in a solid mass. When the temperature of the mixture was about 4–5°, 150 cc. of pure water at 0–1° was added.

One one-hundredth of a mole (1.58 g.) of powdered potassium permanganate was then added in small portions; after addition of the last portion the agitation was continued for about ten minutes, and the temperature maintained at 0–2°. The formation of an intense, cherry-red color was observed. Previously, into the freezing mixture was placed a flask mounted with a Gooch crucible fitted into a rubber ring which was placed on top of the neck of the flask. The cold solution was then filtered with suction through acid-washed asbestos.

The filtrate was transferred to a cooled beaker and ice-cold alcohol, in quantity corresponding to one-half of the potassium trioxalatomanganiate solution, was added. The solution was placed in an efficient cooling mixture (ice and salt) and kept in the dark for about two hours.

The precipitated potassium trioxalatomanganiate was then filtered with suction on a cooled Büchner funnel. The precipitate was washed with ice-cold 50% (by volume) pure alcohol four times, using about 25 cc. for each wash, then with 95% alcohol, absolute alcohol and, finally, three portions of purified ether. The temperature of all solvents used for washing was in the neighborhood of 0°.

The crystals so obtained were sucked dry on a silica crucible, then removed to an evaporating dish and dried at room temperature and atmospheric pressure for twelve hours, and preserved in a colored glass bottle to prevent decomposition by light. It is important that the organic solvents evaporate completely before the bottle is stoppered.

The filtration and washing of the crystals were carried out in the shortest time possible. Based on the data of four experiments, the yield was approximately 50%.

Analysis.—Microscopic examination of the product revealed no inhomogeneity, whereas samples prepared by the other procedures investigated almost invariably contained white crystals of potassium acid oxalate. A complete analysis of the crystals was made by the following methods: (a) total manganese, by gravimetric determination as $Mn_2P_2O_7$; (b) manganese, oxidation equivalent, by liberation of iodine and titration with thiosulfate; (c) oxalate, by titration with permanganate, making allowance for the oxalate oxidized by the manganic ions, as determined in (b); (d) potassium, by decomposition of a sample with sulfuric acid and ignition to constant weight at 500°, subtracting the weight of manganous sulfate calculated from (a); (e) water, by decomposition in a combustion furnace and absorption of the water liberated. The results were as follows, the theoretical values calculated from the formula $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$ being in parentheses: potassium, 24.12 (23.92); manganese 11.19 (11.21); oxalate, 53.90 (53.85); water, 10.9 (11.02).

A sample was examined for iron spectrographically.[8] No iron lines could be detected, the test being sensitive to 0.0001%.

The density of potassium trioxalatomanganiate was determined in a pycnometer, toluene, xylene and ethyl oxalate being used as liquids in different experiments. Three determinations were made with the usual precautions to

---

[7] *Organic Syntheses*, **5**, 59 (1925).

[8] We are indebted to Dr. E. Weiner for conducting this test.

displace adhering air, the results being d^{20}_4 2.148, 2.152, 2.148; mean, 2.149.

Potassium trioxalatomanganiate in the solid state has a deep reddish-purple color. Impure samples often decompose overnight at room temperature, especially if imperfectly dried. We have found that very pure samples keep well even at 20° if protected from the light, and in a refrigerator at $-6°$ no decomposition is apparent after storage for a year or more. The salt is insoluble in alcohol, ether, acetone, toluene and xylene, but is very soluble in water, and very slightly soluble in methyl alcohol. The color of aqueous solutions varies markedly with the concentration. A 0.001 M solution is yellowish-brown; with increasing concentration the solution becomes cherry-red, and concentrated solutions in an oxalate–oxalic acid buffer at pH 5 are deep red with a purplish shade. These color changes are due to the partial replacement of an oxalate ion by water molecules, as shown by spectrophotometric studies which will be reported in the succeeding paper. When a solution is made moderately acid the color changes to a golden-yellow, but rapidly fades, owing to reduction of the manganese. A brown precipitate forms in an acetate buffer if the acidity is decreased appreciably below a pH of 5.

Potassium Dioxalatodiaquomanganiate.—Whereas the trioxalto complexes of cobalt and chromium are very stable with respect to dissociation of the anion, or the replacement of an oxalate group by water molecules, a number of facts made it apparent that the trioxalatomanganiate ion is decidedly less stable in this respect. Addition of silver ions or calcium ions to a solution of the pure salt produces an immediate precipitation of an oxalate, with decomposition of the red salt. Furthermore, the yellow color produced by acidifying the solution is restored to red by addition of an excess of potassium oxalate. Before we discovered the work of Meyer and Schramm we had been successful in isolating the green dioxalatodiaquomanganiate, though considerable work was required before a dependable procedure was developed. Four methods were studied, all of which gave the desired compound in varying degrees of purity.

(a) A concentrated solution of the trioxalato complex at 0° was treated with dilute sulfuric acid until the color changed to a clear golden-yellow; the green dioxalato salt crystallized out upon addition of alcohol. The salt was contaminated with colorless crystals, presumably of potassium acid oxalate.

(b) and (c) Manganous oxalate was oxidized by potassium permanganate in the presence of oxalic acid and potassium oxalate in varying proportions.

(d) The best results were obtained by a simple modification of the procedure developed for making the trioxalato complex. The total reaction is

$$4H_2C_2O_4 + KMnO_4 \longrightarrow K[Mn(H_2O)_2(C_2O_4)_2] + 4CO_2 + 2H_2O \quad (2)$$

The reaction is carried out in one step, and because of the strongly acid character of the solution during the initial stages it is necessary to control the temperature very accurately and to work rapidly according to the following procedure.

Preparation of Potassium Dioxalatodiaquomanganiate.—Eight hundredths of a mole (10.08 g.) of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) was dissolved in 200 cc. of water in a 750-cc. Erlenmeyer flask. The solution was cooled to 1° and 0.02 mole (3.16 g.) of powdered potassium permanganate was added. The mixture was thoroughly agitated for about twenty minutes and the temperature was allowed to rise to 7°, at which temperature the reaction started, as judged by the evolution of carbon dioxide. The flask was immersed quickly in an efficient cooling mixture of ice and salt. The agitation was continued and the temperature was lowered gradually to 0°. When the evolution of gas began to diminish, 25 cc. of ice-cold ethyl alcohol (95%) was added and the temperature was allowed to drop to $-3°$. At this stage the solution was greenish-brown in color, without any red shade. The solution was filtered very quickly through a Gooch crucible with an asbestos mat, which was previously washed and cooled. The filtrate was collected in an externally-cooled flask.

The filtrate was cooled below 0° and 200 cc. of 95% alcohol was added in portions, keeping the temperature below 0°. The solution was allowed to stand in an efficient cooling mixture for about half an hour. If no crystallization had begun at this time the inner wall of the flask was scratched slightly with a stirring rod and the solution allowed to stand at a temperature of -5 to $-10°$ for one hour. Green, lustrous crystals were observed at this time on the bottom of the flask. They were filtered with suction and washed with ice-cold ethyl alcohol (50, 95% and absolute), followed by three washes with ice-cold dry ether. The yield was about 45% of the theoretical.

Anal. The compound was analyzed by the methods described in connection with the trioxalato complex. The results on two samples were as follows, the percentages calculated from the formula $K[Mn(C_2O_4)_2(H_2O)_2] \cdot 3H_2O$ being in parentheses: potassium, 10.76, 10.75 (10.85); manganese, 15.16, 15.22 (15.25); oxalate, 48.70, 48.92 (48.90); water, 25.1 (25.0).

Under the microscope the green crystals appear as well-formed, thin, diamond-shaped plates. The salt dissolves readily in water, giving a golden-yellow solution which rapidly decomposes at room temperature. As the decomposition liberates oxalate ions some trioxalato salt forms in the reaction. The solution does not immediately give a precipitate of calcium oxalate when treated with calcium chloride. Addition of potassium oxalate immediately gives the trioxalato complex. Pink compounds are also formed by addition of chloride ion or fluoride ion. At room temperature the crystals decompose rapidly, as a rule, but in a refrigerator may be preserved.

In one experiment the preparation was conducted by a slight variation of the procedure described. Instead of the theoretical quantity of oxalic acid a 1% excess was used, and only 50 cc. of alcohol was used to precipitate the salt. The product consisted of golden crystals which appeared homogeneous under the microscope. Analysis gave: manganese, 15.1; oxalate, 49.0, 48.7. It is evident that the composition of the two products is identical. The dioxalatodiaquo complex may exist in isomeric *cis* and *trans* forms, and we are of the opinion that the differences observed may be accounted for in this way. The two solids give solutions of the same color, which may indicate that the solution contains both forms in equilibrium. Further work is in progress in this connection.

In a further preparation the reaction mixture was made as nearly anhydrous as would permit the reactions to occur. Eight hundredths of a mole (10.08 g.) of powdered oxalic acid ($H_2C_2O_4\cdot 2H_2O$) was dissolved in 200 cc. of absolute alcohol and cooled to 0°. Two hundredths of a mole (3.16 g.) of powdered potassium permanganate was added. The solution was shaken and a few pieces of ice were added until the solution turned brown and the larger portion of the permanganate went into solution. Then the solution was filtered. The precipitate consisted mainly of unreacted materials. The filtrate was brown in color; 1.12 g. of potassium hydroxide was dissolved in 50 cc. of 95% alcohol. The potassium hydroxide solution was cooled and portions of it were added until a precipitate appeared. The yellowish-green precipitate was filtered off. It was washed in the usual way and analyzed for oxalate and manganic ions. The results follow, the percentages calculated for $K[Mn(C_2O_4)_2(H_2O)_2]$ being in parentheses: manganese, 17.8 (17.91); oxalate, 56.8 (57.5).

The product was apparently the anhydrous form of potassium dioxalatodiaquomanganiate. It was more stable than the trihydrate and remained undecomposed at room temperature for several days. Other characteristics were identical with those of the hydrated form of the salt.

It is claimed by Brintzinger and Eckardt[9] that dioxalato complexes of bivalent central ions often polymerize to double ions in dilute solution. Freezing point measurements accordingly were made on 0.05 *M* solutions of yellow potassium dioxalatodiaquomanganiate by the Beckmann method.[10] The results showed an apparent degree of dissociation of the same magnitude as is commonly found for solutions of uni-univalent salts of the same concentration. The solution is weakly acidic, probably as a result of a slight dissociation according to the reaction $[Mn(C_2O_4)_2(H_2O)_2]^- \rightleftharpoons [Mn(C_2O_4)_2(OH)(H_2O)]^- + H^+$.

Complexes Containing Complex Cations

On account of the high solubility of the potassium salts obtained an effort was made to find some other cation which might give complexes of lower solubility. The alkaline earths and heavy metals are necessarily eliminated because their oxalates also are insoluble. The oxalato anions are relatively large in size, and since it is often true that the solubility of salts with large anions decreases as the cation becomes larger, it was thought likely that compounds containing a complex cation as well as the complex anion might be favorable forms in which to isolate the unstable manganese complexes.

Hexamminecobalti Trioxalatomanganiate, $[(CoNH_3)_6][Mn(C_2O_4)_3]\cdot xH_2O$.—One hundredth of a mole (2.67 g.) of hexamminecobalti chloride $[Co(NH_3)_6]Cl_3$ (yellow) was dissolved in 100 cc. of water at a temperature of 2° and 0.01 mole (4.90 g.) of potassium trioxalatomanganiate dissolved in 50 cc. of water at a temperature of 2° was added. The mixture was shaken, after which a purplish-pink precipitate was observed. The precipitate was filtered off and washed in the usual way; yield 4.8 g. The theoretical yield of anhydrous hexamminecobalti-trioxalatomanganiate is 4.80 g. Upon addition of alcohol to the filtrate, a precipitate formed in small quantity. The mixture was allowed to stand overnight in the refrigerator and the lustrous pink crystals which formed were filtered off and washed with alcohol.

A partial analysis of the first crop of crystals gave manganese 10.6 (10.29), cobalt 10.9 (11.03); oxalate 50.2 (49.44), the values in parentheses being calculated for the trihydrate. The atomic ratio found corresponds to Co: Mn: C_2O_4 = 0.96:1.00:2.96, the percentage values lying between those for the dihydrate and the trihydrate.

The dioxalatodiaquomanganiate anion also unites with complex cations to form sparingly soluble double complexes. With *cis*-dinitrotetrammine cobalti ion an olive-yellow precipitate was obtained. The product was heterogeneous under the microscope, however, and was not subjected to analysis.

Note on Potassium Dimalonatodiaquomanganiate

Meyer and Schramm[5] prepared their complex manganiates by using manganic hydroxide or manganese dioxide as the source of manganese. Their procedures gave impure products in many instances, and they report that they were not able to obtain potassium dimalonatodiaquomanganiate in a form suitable for analysis. We have conducted several experiments in which it was hoped that the greater stability of malonic acid toward oxidation would permit isolation of a type of hydroxo complex that we have not been able so far to obtain in pure form in the oxalate series. It was found that suitable modification of our procedure, in which potassium permanganate is used, easily produces pure crystals of the potassium salt, $K[Mn(C_3H_2O_4)_2(H_2O)_2]\cdot 2H_2O$.

Four procedures were investigated in which malonic acid, potassium permanganate and, in two cases, potassium carbonate were mixed in various proportions in aqueous solution at 0°. In all cases the same product was obtained, the yield being highest (80%) when stoichiometric proportions were used according to the equation

$$5CH_2(COOH)_2 + 2KMnO_4 \longrightarrow 2K[Mn(C_3H_2O_4)_2(H_2O)_2] + 3CO_2 + 2H_2O$$

The reactions were carried out at about 0° in solutions containing 0.01 mole of permanganate with the other reagents in 100 cc. of water. To precipitate the crystals 50 cc. of alcohol was also present. The average of four closely concordant analyses for manganese was as follows, the value calculated for the dihydrate being in parentheses: Mn, 14.85% (14.83). Potassium and water were determined on one sample: K, 10.4 (10.57); H_2O, 2.63 (2.7). The dark-green crystals dissolve readily in water to give an unstable yellow solution, as reported for the other salts by Meyer and Schramm. The salt may be recrystallized from cold 0.05 *M* malonic acid by addition of alcohol.

---

(9) Brintzinger and Eckardt, *Z. anorg. allgem. Chem.*, **224**, 93 (1935).

(10) We are indebted to Mr. J. T. Grey, Jr., for making the measurements.

Summary

1. A procedure has been developed whereby potassium trioxalatomanganiate may be prepared spectroscopically free from iron.

2. Potassium dioxalatodiaquomanganiate has been prepared in the pure crystalline state. Two forms of the trihydrate have been obtained, as well as the anhydrous salt.

3. It has been shown that these manganiate ions form sparingly soluble salts with complex cations.

4. Pure potassium dimalonatodiaquomanganiate has been prepared and certain of its properties have been determined.

BUFFALO, N. Y. RECEIVED JUNE 19, 1936

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

Equilibrium between the Trioxalatomanganiate and Dioxalatodiaquomanganiate Ions

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

In spite of the enormous number of transformations among complex compounds that have been developed in the course of the classic researches of Werner and his successors, very few of such reactions have been investigated quantitatively from the standpoint of chemical equilibrium. The complexes of the metals that have been most fully studied are, as a rule, so stable with respect to dissociation that readily measurable equilibria are comparatively rare. Such measurements as have been made concern principally the dissociation of solid ammine complexes or the instability constants of such relatively stable complexes as the silver–ammonia or silver–cyanide ions in solution. In a few cases the acidic dissociation of aquo complex ions has also been studied.[1] Investigations of affinity in the complex compounds are desirable on account of the renewed interest in the question as to the type and strength of the chemical bonds in such substances.

Meyer and Schramm[2] observed that the trioxalatomanganiate ion and the dioxalatodiaquomanganiate ion are convertible one into the other according to the equation

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

That a measurable equilibrium is established rapidly is evident from the color changes observed in aqueous solutions of the trioxalatomanganiates. A concentrated aqueous solution is ordinarily described as cherry-red. We have found that the color is perceptibly changed to a more purplish-red upon addition of an oxalate–oxalic acid buffer at pH 4.5. As an aqueous solution is diluted its color changes steadily; in 0.001 M solution the color is brown, but may be restored to red by addition of an excess of the oxalate buffer. The dioxalatodiaquomanganiate ion reacts immediately with the oxalate ion to produce the trioxalato complex. In this respect the dioxalato ion contrasts with the dimalonato ion, which is very incompletely converted to the trimalonato ion. The dioxalatodiaquomanganiate ion itself has a golden-yellow color in cold aqueous solution, but the solution is acid and soon becomes turbid. This effect is no doubt due to an acidic ionization of the water molecules in the complex, whereby a sparingly soluble hydroxo complex is formed. We have found that the solution in 0.01 M nitric acid remains clear and is stable enough for our purposes. The nitric acid evidently suppresses the ionization, giving the pure color of the aquo complex ion.

The method of determining the equilibrium concentrations consisted in a spectrophotometric analysis of solutions of the trioxalatomanganiate in water at various concentrations and also in various oxalate–oxalic acid buffer mixtures. Equilibrium was also approached from the dioxalatodiaquomanganiate side of the reaction. As has been found by Uspensky and his collaborators[3] in a number of cobaltic and chromic complexes, when water molecules replace an acido group within a complex ion the maximum absorption in the visible region is displaced in the direction of shorter wave lengths. In the oxalatomanganiates

---

[1] Brönsted and King, *Z. physik. Chem.*, **130**, 699 (1927).

[2] Meyer and Schramm, *Z. anorg. allgem. Chem.*, **157**, 190 (1926).

[3] Uspensky and others, *Trans. Inst. Pure Chem. Reagents, U. S. S. R.*, **13**, 1 (1933).