corresponding $FeCl^{2+}$–Fe^{2+} reaction. This difference in rates is small and may be due to differences in the standard free energy changes of the reactions. This suggests that spin multiplicity restrictions have, at most, a small effect on the rate of the $CoCl^{2+}$–Co^{2+} electron-transfer reaction.

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The Crystal Structure, Visible, and Ultraviolet Spectra of Potassium Hexachloromanganate(IV)[1]

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Powder diffraction patterns of potassium hexachloromanganate(IV) can be indexed on the basis of a cubic cell with a_0 = 9.6445 ± 0.0020 Å. Systematic extinctions indicate that potassium hexachloromanganate(IV) is isostructural with potassium hexachloroplatinate(IV) and has the antifluorite structure [space group No. 225, Fm3m-O_h^5; with four Mn in (a) 000 + F.C.; eight K in (c) $\pm(^1/_4{}^1/_4{}^1/_4)$ + F.C.; and 24 Cl in (e) $\pm(x00, 0x0, 00x)$ + F.C.]. Intensity data were collected, and the structure was refined by the method of least squares. Individual temperature parameters B_{Mn}, B_K, and B_{Cl} were determined to be 1.9 ± 0.3, 3.0 ± 0.4, and 2.55 ± 0.1 Å.^{2}, respectively, and the single structural parameter, x, was determined to be 0.2360 ± 0.0004. The Mn–Cl bond distance is 2.276 ± 0.004 Å., and the K–Cl bond distance is 3.412 ± 0.004 Å. The ammonium (a_0 = 9.80 ± 0.02 Å.), rubidium (a_0 = 9.82 ± 0.02 Å.), cesium (a_0 = 10.17 ± 0.02 Å.), and tetramethylammonium (a_0 = 12.70 ± 0.02 Å.) hexachloromanganate(IV) salts were also prepared and have similar structures. The visible and ultraviolet spectra of potassium hexachloromanganate(IV) were determined and are discussed.

Introduction

Potassium hexachloromanganate(IV), K_2MnCl_6, was first prepared by Meyer and Best[2] in 1899. Weinland and Dinkelacker[3] later prepared the compound by the reaction of potassium permanganate with fuming hydrochloric acid

$$2KMnO_4(s) + 16HCl \longrightarrow K_2MnCl_6(s) + 4Cl_2(g) + 8H_2O + Mn^{2+} + 2Cl^-$$

and also reported the preparation of the ammonium and rubidium salts. The hexachloromanganate(IV) salts are described as black solids which rapidly decompose on standing. Individual crystals appear "deep dark red" under a microscope. The magnetic susceptibility of K_2MnCl_6 has been determined,[4] but apart from this the hexachloromanganate(IV) salts have not been studied.

Very few manganese compounds in which the manganese atom has an oxidation number of +4 are known. It is therefore of interest to characterize these compounds further. Although the hexachloromanganate(IV) salts are not stable for long periods, it was possible to determine the structure of K_2MnCl_6 by X-ray powder techniques. The visible and ultraviolet spectra of K_2MnCl_6, as well as the unit cell dimensions of the ammonium, rubidium, cesium, and tetramethylammonium salts, were also obtained.

Experimental Section

Analyses.—Available chlorine, the chlorine liberated when the manganese in higher oxidation states is reduced to manganous ion by chloride ion, was determined by an iodometric titration. An acidic potassium iodide solution was added to a sample of the hexachloromanganate(IV) salt, and the liberated iodine was titrated with a standard sodium thiosulfate solution. The solution remaining from the available chlorine analysis was analyzed for manganese by adjusting the pH to 10 and titrating with a standard ethylenediaminetetraacetic acid solution using the "copper–PAN system" as an indicator.[5]

Preparation of Compounds.—Potassium hexafluoromanganate(IV) was prepared by the reduction of potassium permanganate with ether in a solution of hydrofluoric acid.[6]

Potassium hexachloromanganate(IV) was prepared by the method of Weinland and Dinkelacker.[3] The following detailed procedure gives good results.

Concentrated hydrochloric acid (50 ml.) was cooled to 0° and saturated with hydrogen chloride gas. Finely powdered potassium permanganate (5 g.) was added; a vigorous reaction occurred, and the temperature rose to 15°. The solution was allowed to stand for 15 min. at 15° and then was poured into a sintered-glass funnel. The black solid which collected was thoroughly washed with glacial acetic acid and dried by drawing air through it for 30 min. The yield of potassium hexachloromanganate(IV) was 4.5 g., 82% based on potassium permanganate.

Anal. Calcd. for K_2MnCl_6: available Cl, 20.5; Mn, 15.9; mole ratio available Cl/Mn, 2.00. Found 1 hr. after preparation: available Cl, 20.1; Mn, 15.7; mole ratio of available Cl/Mn, 1.98. Found 16 hr. after preparation: available Cl, 19.3; Mn, 15.3; mole ratio of available Cl/Mn, 1.96. Found 96 hr. after preparation: available Cl, 19.1; Mn, 15.9; mole ratio of available Cl/Mn, 1.87.

The ammonium, rubidium, cesium, and tetramethylammonium salts of hexachloromanganate(IV) were prepared by adding the

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[1] Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965.

[2] R. J. Meyer and H. Best, *Z. anorg. allgem. Chem.*, **22**, 169 (1899).

[3] R. F. Weinland and P. Dinkelacker, *ibid.*, **60**, 173 (1908).

[4] S. S. Bhatnagar, B. Prakash, and J. C. Maheshwari, *Proc. Indian Acad. Sci.*, **A10**, 150 (1939).

[5] H. Flaschka and H. Abdine, *Chemist-Analyst*, **45**, 58 (1956).

[6] W. G. Palmer, "Experimental Inorganic Chemistry," Cambridge University Press, London, 1954, p. 484.

requisite chloride to a solution of calcium permanganate in fuming hydrochloric acid.[3] The preparation of cesium hexachloromanganate(IV) is outlined below; the preparation of the ammonium, rubidium, and tetramethylammonium salts employed the same method, and their analyses gave similar results.

Concentrated hydrochloric acid (50 ml.) was cooled to −20°, and approximately 20 g. of anhydrous hydrogen chloride was added to the solution. A slurry of 5 g. of calcium permanganate tetrahydrate[7] and 2 g. of cesium chloride in 15 ml. of water was added, a vigorous reaction occurred, and the temperature rose to 15°. The solution was allowed to stand at that temperature for 15 min. and was then poured into a sintered glass funnel. The black solid which collected was thoroughly washed, first with glacial acetic acid and then with acetonitrile. It was dried by drawing air through it for a few minutes; the yield of cesium hexachloromanganate(IV) was 3.2 g., 50% based on cesium chloride.

Anal. Calcd. for Cs_2MnCl_6: available Cl, 13.3; Mn, 10.3. Found: available Cl, 13.2; Mn, 10.3.

X-Ray Measurements.—X-Ray powder photographs of the hexachloromanganate(IV) salts were obtained with a 14.32-cm. diameter camera employing nickel-filtered Cu Kα radiation. The samples were contained in 0.3-mm. Lindemann glass capillaries. The photographs could all be indexed on the basis of face-centered cubic lattices; the lattice parameters and their estimated probable errors are reported in Table I. The lattice parameter for K_2MnCl_6 was determined by a plot of a_0 *vs.* $^1/_2$ $(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$; the probable error was assigned[8] to be 0.0020 Å. although the reproducibility of the experiments was considerably better than this.

Table I

The Cubic Cell Parameter of Some Hexachloromanganate(IV) Salts at 25°

Salt	a_0, Å.
K_2MnCl_6	9.6445 ± 0.0020
$(NH_4)_2MnCl_6$	9.80 ± 0.02
Rb_2MnCl_6	9.82 ± 0.02
Cs_2MnCl_6	10.17 ± 0.02
$[N(CH_3)_4]_2MnCl_6$	12.70 ± 0.02

Table II

The Observed and Calculated Intensities of the Powder Pattern of K_2MnCl_6

hkl	$10^{-4}I_o$	$10^{-4}I_c$	w
(111)	1060	1060	1
(200)	204	263	1
(220)	306	319	1
(311)	225	245	2
(222)	1870	1880	1
(400)	1770	1740	1
(331)	24	28	4
(420)	72	78	3
(422)	126	111	3
(333), (511)	236	209	2
(440)	810	798	1
(531)	159	140	2
(600), (442)	40	33	3
(620)	35	53	4
(533)	22	22	4
(622)	319	293	2
(444)	231	199	2
(711), (551)	88	81	3
(640)	11	17	4
(642)	41	40	4
(731), (553)	38	36	4
(800)	70	73	4
(733)	2*U*	1	1
(820), (644)	5	14	5
(822), (660)	10	12	5
(555), (751)	27	27	4
(662)	74	73	3
(840)	188	171	2
(911), (753)	24	27	4
(842)	8	6	4
(664)	5	8	4
(931)	36	26	4
(844)	130	119	3
(933), (771), (755) (10,00), (860)	19	20	2
(10,20), (862)	15	13	4
(951), (773) (10,22), (666) (953)	113	97	2
(10,40), (864)	36	44	2
(10,42)	6	12	4
(11,11), (775)	2*U*	. . .	1
(880)	38	45	3
(11,31), (971), (955) (10,44), (882)	44	49	2
(10,60), (866)	7	12	4
(11,33), (973) (10,62)	43	74	2
(12,00), (884)	106	132	1

Intensity measurements of the potassium hexachloromanganate(IV) powder pattern were obtained on a General Electric XRD5 diffractometer fitted with a proportional counter (General Electric SPG-6). As potassium hexachloromanganate(IV) is not stable, the compound was prepared and analyzed, and the intensity data were recorded within a period of 8 hr. Nickel-filtered Cu Kα radiation was employed, and the sample was loaded in a Bakelite tray. The output of a ratemeter was recorded on a chart, all reflections were recorded on the same scale, and the intensity of the five strongest reflections was reduced with a calibrated set of nickel-foil filters. The area above the background under each peak was determined with a planimeter, and these areas (multiplied by filter factors for the five strongest reflections) are the experimental relative intensities. Experimental intensities, multiplied by a scale factor, are I_o in Table II.

Visible and Ultraviolet Spectra.—A reflectance spectrum of a mixture of potassium hexachloromanganate(IV) and magnesium oxide over the range 1200–400 mμ (8300–25,000 cm.$^{-1}$) was obtained with a Beckman DK-2 spectrophotometer.

Visible and ultraviolet absorption spectra of potassium hexafluoromanganate(IV) and potassium hexachloromanganate(IV) were obtained over the range 750–230 mμ (13,000–43,000 cm.$^{-1}$) with a Perkin-Elmer Model 202 spectrophotometer. The samples were mulled with a fluorocarbon grease[9] and held between quartz plates. Samples of K_2MnCl_6 and K_2MnF_6 were run under as nearly identical conditions as possible so that a qualitative comparison of the relative intensities of the absorption bands for the two compounds could be made. The observed absorption bands and their relative intensities are reported in Table III; the spectrum of potassium hexafluoromanganate(IV) is in good agreement with the reported reflectance spectrum.[10]

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(7) Carus Chemical Co., Inc., LaSalle, Ill.

(8) W. Parrish and A. J. C. Wilson in "International Tables for X-Ray Crystallography," Vol. II, J. S. Kasper and K. Lonsdale, Ed., The Kynoch Press, Birmingham, England, 1959, p. 216.

(9) Kel-F No. 90 supplied by the Minnesota Mining and Manufacturing Co., St. Paul, Minn.

(10) C. K. Jørgensen, *Acta Chem. Scand.*, **12**, 1539 (1958).

TABLE III

THE VISIBLE AND ULTRAVIOLET SPECTRA OF K_2MnCl_6 AND K_2MnF_6

Compd.	Type of spectrum	ν_{max}, cm.$^{-1}$	Rel. intens.
K_2MnF_6	Absorption	21,800	Weak
		27,800	Weak
K_2MnCl_6	Absorption	15,400	Very strong
		27,400	Strong
		33,300	Strong
K_2MnCl_6	Reflectance	16,600	Very strong

The Determination of the Structure of K_2MnCl_6

The powder pattern of potassium hexachloromanganate(IV) could be indexed on the basis of a face-centered cubic lattice. It seemed probable that it was isostructural with potassium hexachloroplatinate(IV) and has the antifluorite structure [space group No. 225, Fm3m-O_h^5; with four Mn in (a) 000 + F.C.; eight K in (c) ± ($^1/_4{}^1/_4{}^1/_4$) + F.C.; and 24 Cl in (e) ± (x00, 0x0, 00x) + F.C.]. Since the agreement between observed and calculated intensities is very good, this assumption is justified.

A preliminary determination of the structural parameter, x, and over-all temperature factor, B, was obtained by comparing structure factors, obtained from the intensities for the 26 observed independent reflections in Table II, with calculated structure factors. The approximate values x = 0.238 and B = 2.7 Å.^{2} were obtained.

The intensity data were then refined by the method of least squares.[11] A full-matrix, least-squares program was written for use on the G.E. 225 computer at the Center for Documentation and Communication Research at Western Reserve University. The quantity $\Sigma w(I_o - I_c)^2$ was minimized. Values of I_c, on an arbitrary scale, were obtained from the formula

$$I_c = \Sigma 4(\sin\theta)^{-1}LPJ|F|^2$$

where L and P are the Lorentz and polarization factors and J is the multiplicity. The summation is taken over all of the reflections contributing to a single intensity measurement. The structure factor, F, was corrected for temperature by multiplying the scattering factors for the individual atoms by terms of the form exp $(-B \sin^2\theta/\lambda^2)$ where the B values are all the same if the over-all temperature factor is being considered or differ for each type of atom if individual temperature factors are being considered. The scattering factors used for Mn^{4+}, K^+, and Cl^- were taken from the International Tables.[12]

TABLE IV

ATOMIC COORDINATES, THERMAL PARAMETERS (Å.^{2}), AND THEIR STANDARD DEVIATIONS

	B_{Mn}	σ_{Mn}	B_K	σ_K	B_{Cl}	σ_{Cl}	x	σ_x	$\frac{\Sigma w(I_o - I_c)^2}{44 - n}$ [a]	$\frac{\Sigma\lvert I_o - I_c\rvert}{\Sigma I_o}$
1st calcn.	2.8	0.1	2.8	0.1	2.8	0.1	0.2366	0.0006	8.4×10^{10}	0.074
2nd calcn.	1.9	0.3	3.0	0.4	2.55	0.1	0.2360	0.0004	4.8×10^{10}	0.056

[a] n = the number of parameters being considered in the calculation.

The observed intensities were obtained from the experimental intensities by multiplying by a scale factor K where $I_o = KI_{exptl}$ and $K = \Sigma I_c/\Sigma I_{exptl}$.

The weighting factors, w, are ideally the reciprocal of the variance squared,[11] $\sigma^2(I_o)$. The square of the variance was estimated from the expression[13] $\sigma^2 = E + 2B$, where E is the number of counts in the peak and B is the number of counts in the background. Weighting factors are reported in Table II; they do not vary greatly as the background was high. Unobserved reflections (designated U in Table II) have arbitrarily been assigned an intensity of half the minimum observed and a weight of 1.

In the first least-squares calculation the structural parameter, x, and over-all temperature parameter, B, were refined. Normal equations were obtained as described by Whittaker and Robinson[11] in which the trial parameters were x = 0.238 and B = 2.7 Å.^{2}. The refined parameters and their estimated standard deviations are reported in Table IV; the standard deviations were estimated from the inverse of the matrix.[11]

A second least-squares calculation was carried out in which four parameters, the structural parameter and individual temperature parameters, were refined. The results of the first least-squares calculation were used as trial parameters. After several cycles of least-squares calculation, the results reported in Table IV were obtained. The values of I_c reported in Table II were obtained using the refined parameters from the second least-squares calculation.

The final value of the Mn–Cl bond distance is 2.276 ± 0.004 Å., while the K–Cl distance is 3.412 ± 0.004 Å.

Discussion

Crystal Structure of K_2MnCl_6.—The structure of potassium hexachloromanganate(IV) is one in which the K^+ ions and octahedral $MnCl_6^{2-}$ ions occupy, respectively, the F^- and Ca^{2+} ion positions of the fluorite structure. The $MnCl_6^{2-}$ ions are at the corners and the centers of the faces of the cubic unit cell and are surrounded by eight K^+ ions at the corners of a cube. In the isostructural hexachloroplatinate(IV) salts the Pt–Cl bond distance[14a] averages 2.30 Å. Pauling[14a] assigned the chlorine atom a covalent radius of 0.99 Å. and the Pt(IV) atom an octahedral covalent radius of

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(11) E. Whittaker and G. Robinson, "The Calculus of Observations," 4th Ed., Blackie and Son Ltd., London, 1944, pp. 209–259.

(12) C. H. MacGillavry, G. D. Rieck, and K. Lonsdale, Ed., "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1A, p. 202.

(13) W. Parrish, *Philips Tech. Rev.*, **17**, 206 (1955/1956).

(14) (a) L. Pauling "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960: (a) pp. 244–251; (b) pp. 514, 518.

1.31 Å. A similar interpretation of bonding in potassium hexachloromanganate(IV) would give the Mn(IV) atom an octahedral covalent radius of 1.29 Å. Actually, the Mn–Cl bond distance corresponds quite closely to that expected for ionic bonding. The Mn^{4+} ion has been assigned[14b] a radius of 0.54 Å., and the Cl^- ion a radius of 1.81 Å. The sum, 2.35 Å., is in reasonably good agreement with the observed distance of 2.28 Å. No conclusion about the extent of covalent bonding in K_2MnCl_6 can be reached from the X-ray measurements alone.

The Visible and Ultraviolet Spectra of K_2MnCl_6.—The results of the structure determination and magnetic susceptibility measurements[4] indicate that the hexachloromanganate(IV) ion is an octahedral high-spin complex. A consideration of its visible and ultraviolet spectra might give more information about the octahedral ligand field of chlorine. As a d^3 ion the spectra and magnetic behavior of Mn(IV) complexes should resemble those of V(II) and Cr(III) complexes.[15] The ligand field parameter, $10Dq$, for the hexachlorochromate(III) ion has been reported as 13,180 cm.$^{-1}$ [16] and 13,800 cm.$^{-1}$ [17], while $10Dq$ for the hexafluorochromate ion has been reported[17] to be 15,200 cm.$^{-1}$. The value of $10Dq$ is shifted about 2000 cm.$^{-1}$ to longer wave lengths in going from the hexafluorochromate(III) ion to the hexachlorochromate(III) ion. Potassium hexafluoromanganate(IV) has been reported[10] to have a $10Dq$ of 21,750 cm.$^{-1}$, and one might suppose that $10Dq$ for potassium hexachloromanganate(IV) would be about 19,700 cm.$^{-1}$. One can predict the frequencies of the transitions expected for potassium hexachloromanganate(IV) using this value for $10Dq$ and either the Orgel[18] or Liehr[19] diagram for Cr(III), *i.e.*, ${}^4A_{2g} \rightarrow {}^4T_{2g}$ at 19,700 cm.$^{-1}$; ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ at 28,000 cm.$^{-1}$; and ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$ at 43,000 cm.$^{-1}$. While three absorption bands are observed for potassium hexachloromanganate(IV) the positions of the maxima are not in very good agreement with the values predicted above.

It seems probable that the observed spectrum of potassium hexachloromanganate(IV) is due, at least partially, to electron transfer. Electron-transfer spectra in coordination compounds have been discussed by Dunn,[20] and a theoretical treatment has been given by Jørgensen.[21] Three facts are consistent with the supposition that the absorption spectrum of potassium hexachloromanganate(IV) is due to electron transfer.

(1) The absorption maxima in the visible and ultraviolet spectra of potassium hexachloromanganate(IV) are very intense when compared to the absorption maxima of potassium hexafluoromanganate(IV).

(2) Jørgensen[21] has pointed out that, in the hexahalo complexes of the 4d- and 5d-transition elements, the charge-transfer bands are shifted 28,000 cm.$^{-1}$ toward longer wave lengths in going from fluorine to chlorine complexes. Thus, the observation of charge-transfer spectra in potassium hexachloromanganate(IV) and not in potassium hexafluoromanganate(IV) is not inconsistent.

(3) Orgel has noted[22] that, if a charge-transfer band occurs at long wave lengths, the energy which must be supplied to achieve a permanent oxidation–reduction reaction is small, and a complex containing a slightly more oxidizable anion might undergo spontaneous reaction. This behavior is observed in cupric ion–bromide ion and cupric ion–iodide ion solutions, the former solution having a charge-transfer band at long wave lengths and the latter solution undergoing spontaneous reaction. This same behavior is observed in the case of potassium hexachloromanganate(IV) and potassium hexabromomanganate(IV); the former has an intense band at long wave lengths, and the latter has never been reported. The higher oxidation states of manganese are spontaneously reduced to the manganous ion in the presence of bromide ion.

One might conclude that the absorption band of potassium hexachloromanganate(IV) at 15,400 cm.$^{-1}$ and its reflectance spectrum are due to charge transfer. It is more difficult to assign the bands observed at shorter wave lengths. Other charge-transfer bands would be expected and might obscure the d–d transitions; however, the shorter wave length bands could be due to ususually intense d–d transitions.[23]

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[15] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 233, 235, 250.

[16] W. E. Hatfield, R. C. Fay, C. E. Pfluger, and T. S. Piper, *J. Am. Chem. Soc.*, **85**, 265 (1963).

[17] C. E. Schaffer and C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **8**, 143 (1958).

[18] L. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).

[19] A. D. Liehr, *J. Phys. Chem.*, **67**, 1314 (1963).

[20] T. M. Dunn, *Mod. Coord. Chem.*, 268 (1960).

[21] C. K. Jørgensen, *Advan. Chem. Phys.*, **5**, 75 (1963).

[22] L. Orgel, "An Introduction to Transition-Metal Chemistry: Ligand Field Theory," John Wiley and Sons, Inc., New York, N. Y., 1960, p. 99.

[23] Note Added in Proof.—It has recently been brought to the author's attention that Sartori, Cervone, and Cancellieri[24] have published the spectrum of a solution of potassium hexachloromanganate(IV) in concentrated hydrochloric acid. The reported spectrum is not in agreement with the present work; however it is similar to those observed for solutions of Mn(III) in hydrochloric acid.[25] Unpublished work from our laboratory indicates that on standing in moist air the hexachloromanganate(IV) salts are rapidly converted to the corresponding aquopentachloromanganate(III) salts.

[24] G. Sartori, E. Cervone, and P. Cancellieri, *Atti Acad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. Nat.*, **35**, 226 (1963).

[25] J. A. Ibers and N. Davidson, *J. Am. Chem. Soc.*, **72**, 4744 (1950).