Table III. Kinetic Results with Excess Bromate[a]

$10^3[BrO_3^-]_0$, M	$[HClO_4]$, M	k_a, M^{-1} sec^{-1} [b]
1.70	1.93	3.31 ± 0.03
3.16	1.92	3.34 ± 0.04
3.16	1.42	2.53 ± 0.01
5.29	0.947	1.55 ± 0.01
3.16	0.947	1.51 ± 0.01
4.24	0.716	1.07 ± 0.02
7.37	0.474	0.719 ± 0.017
7.90	0.332	0.477 ± 0.002
7.90[c]	0.190	0.221 ± 0.001
7.90[d]	0.190	0.203 ± 0.003
7.90	0.190	0.245 ± 0.004
7.90[e]	0.190	0.364 ± 0.002
0.45[f]	3.55	17.2 ± 0.2
3.16[g]	1.92	2.02 ± 0.01
5.29[h]	1.92	1.25 ± 0.01
7.90[i]	1.92	0.856 ± 0.016

[a] $[HClO_2]_0 = 6.33 \times 10^{-4}$ M and $[CH_2{=}CHCH_2OH]_0 = 2.63 \times 10^{-3}$ M. $T = 25.0°$ and $I = 1.93$ M ($LiClO_4$) unless otherwise indicated. [b] Uncertainties are average deviations of replicate experiments. [c] $I = 0.19$ M. [d] $I = 0.95$ M. [e] $I = 3.06$ M. [f] $I = 3.55$ M. [g] $T = 17.0°$. [h] $T = 10.0°$. [i] $T = 5.0°$.

shown in (IV) comes from a study of the disproportionation of chlorous acid[6] and a variety of evidence that suggests that bromous acid prefers to oxidize in a two-equivalent path whenever possible.[2,7,8,10] Bromate ion also normally acts as a two-equivalent oxidant. Its failure to do so in the present system may result from a facile production of a $BrClO_4$ intermediate in reaction I, analogous to the probable formation of Br_2O_4 in reaction 1.[4] A difficult question to suitably answer, however, is why $BrClO_4$ would dissociate rather than undergo the redox reaction III. It may be that both of these reactions occur, and our reaction scheme is oversimplified.

The result that k_c/k_b is near unity at high acidities is consistent with the assumption that bromine dioxide is a very reactive species and does not discriminate between chlorine dioxide and chlorous acid. However, the hydrogen ion dependence of K is not predictable from reaction scheme I-IV. A possibility is that bromine dioxide reacts much more rapidly with chlorite ion than chlorous acid.

Registry No. BrO_3^-, 15541-45-4; $HClO_2$, 13898-47-0; ClO_2, 10049-04-4; ClO_3^-, 14866-68-3.

Appendix I

Let eq 9 be expressed as

$$d(By)/dB = -{}^3/_2 - K/y$$

where $y = A/B$, $A = [HClO_2]$, $B = [ClO_2]$, and $K = k_c/k_b$. Then, since $A_\infty = 0$ at the plateau (see Figure 1) and $B_0 > 0$ if ClO_2 is added

$$\int_{B_0}^{B_\infty} -d(\ln B) = \int_{y_0}^{0} [y/(K + 3y/2 + y^2)]\ dy$$

This equation can be integrated in closed form and rearranged to yield eq 11.

Appendix II

Let eq 10 be expressed as

$$d(Ay)/dA = -1/({}^3/_2 + Ky)$$

where $y = B/A$, $A = [HClO_2]$, $B = [ClO_2]$, and $K = k_c/k_b$. Then, since $y_0 = 0$ with no added ClO_2 as in the kinetic experiments

$$\int_{A_0}^{A} -d(\ln A) = \int_0^Y [({}^3/_2 + Ky)/(1 + 3y/2 + y^2)]dy$$

This equation can be integrated and rearranged to yield eq 12. Equations 11 and 12 are valid provided $9/4 - 4K > 0$; this happens to be the case when $[H^+] \leqslant 2.0$ M for the present system. For the experiments conducted in 3.55 M $HClO_4$, $9/4 - 4K < 0$. The integrated expression is then different from eq 12 and involves arctangents. This latter expression was used for those experiments.

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Electron Spin Resonance and Optical Spectra of the Hexachloromanganate(IV) Ion

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The single-crystal optical spectrum of Mn(IV) doped into K_2SnCl_6 has been measured as well as the esr of the polycrystalline Mn(IV) in K_2SnCl_6. The Racah parameter B was evaluated at 584 cm^{-1} and $10Dq$ was shown to be 18,240 cm^{-1}. Variable-temperature studies show that Mn(IV) is thermally unstable in the $SnCl_6^{2-}$ lattice and is reduced to Mn(II), probably through Mn(III). Evidence for Mn(III) in the optical spectrum is discussed.

Introduction

Mn(IV) has a very restricted chemistry and relatively little has been reported on the spectra of its complexes either in solution or in the crystalline state.[2] Most extensively treated has been the MnF_6^{2-} ion, whose absorption and emission spectra have been quite thoroughly investigated.[3-8] Reflectance spectra of the analogous chloro complex have been studied by Moews[9] and by Jezowska-Trzebiatowska and coworkers,[10] who also studied the solution spectrum. No report of the crystal spectrum of $MnCl_6^{2-}$ at low temperature

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[1] (a) Canisius College. (b) State University of New York at Buffalo.

[2] W. Levason and C. A. McAuliffe, *Coord. Chem. Rev.*, 7, 353 (1972).

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[6] M. J. Reisfeld, N. A. Matwiyoff, and L. B. Asprey, *J. Mol. Spectrosc.*, 39, 8 (1971).

[7] D. S. Novotny and G. D. Sturgeon, *Inorg. Nucl. Chem. Lett.*, 6, 455 (1970).

[8] G. C. Allen, G. A. M. El-Sharkarwy, and K. D. Warren, *Inorg. Nucl. Chem. Lett.*, 5, 725 (1969).

[9] P. C. Moews, Jr., *Inorg. Chem.*, 5, 5 (1966).

[10] B. Jezowska-Trzebiatowska, S. Wajda, M. Baluka, L. Natkaniec, and W. Wojciechowski, *Inorg. Chim. Acta*, 1, 205 (1967).

has yet appeared. We here report an optical and electron spin resonance (esr) spectral study at ambient and liquid nitrogen temperatures of the $MnCl_6^{2-}$ ion and its reduction products in the K_2SnCl_6 matrix.

Experimental Section

Mixed single crystals of $K_2Sn(Mn)Cl_6$ of optical quality can be obtained in several ways.

(1) Solid $KMnO_4$ is dissolved in a saturated solution of K_2SnCl_6 in 6 *M* HCl; the Mn(VII) is reduced by HCl, and upon slow evaporation of the solution rather large mixed crystals form. The extent of substitution and the color of the crystals depend on the amount of $KMnO_4$ added and the rate of crystallization. If the crystallization is slow, less substitution will occur, since Mn(IV) in 6 *M* HCl is slowly reduced on standing.

(2) If $MnCl_2$ is also added to a saturated solution of K_2SnCl_6 in 6 *M* HCl along with $KMnO_4$, a higher Mn(IV) concentration can be maintained in solution for a longer period, but the resulting crystals are more contaminated with Mn(II). For example, in one preparation using this method 0.58 g of $KMnO_4$ and 2.90 g of $MnCl_2 \cdot 4H_2O$ (a 1:4 molar ratio) were dissolved in about 50 ml of a saturated solution of K_2SnCl_6 in 6 *M* HCl. Upon slow evaporation of the solution red crystals separated. In other similar preparations more dilute crystals were prepared by using smaller amounts of $KMnO_4$ and $MnCl_2 \cdot 4H_2O$ in about the same amount of solution.

(3) Slightly substituted crystals can with difficulty also be obtained by adding MnO_2 to concentrated HCl, decanting the resulting solution into a saturated solution of K_2SnCl_6 in 6 *M* HCl, and allowing the mixture to evaporate slowly. During the evaporation process it may be necessary to make further additions of the MnO_2-HCl decantate in order to keep an observable amount of Mn(IV) in solution.

K_2MnCl_6 was prepared as described by Moews.[9]

All optical spectra were recorded at approximately 300°K and at 77°K on a Cary 14 spectrophotometer employing a cold-finger type cell in which the crystal was cooled by conduction using liquid nitrogen as coolant.

X-Band esr spectra were determined at various temperatures intermediate between 77 and 300°K by employing a Varian variable-temperature control apparatus with liquid nitrogen as coolant. A Varian V-4502-19 spectrometer was used in conjunction with a Magnion proton oscillator gauss meter and a Hewlett-Packard frequency meter to obtain accurate measurements of the magnetic field and microwave frequency. Spectra were scanned slowly to determine the hyperfine parameters accurately.

Since the hyperfine lines are on the order of 70 G, the high-field approximation cannot be applied rigorously and second-order corrections should be employed. The perturbation of the Zeeman transition resulting from the hyperfine interactions was corrected by means of the equations

$$h\nu = g\beta H_0$$

$$H_0 = H_\mathrm{m} + \langle a\rangle m_I + \frac{\langle a\rangle^2}{2H_0}[I(I+1) - m_I^2]$$

where H_m is the magnetic field position of the esr line due to the component m_I of the nuclear spin I, ν is the klystron frequency, and $\langle a\rangle$ is the hyperfine splitting constant. The hyperfine splitting constants were determined by the positions of the third and fourth, second and fifth, and first and sixth lines.

Results and Discussion

The crystals obtained by the methods outlined above vary from a ruby red to an off-white color depending on the degree of substitution. The spectra of all these crystals are similar but not identical (see below). Not all bands are observed in all crystals, since the relative intensities of the absorptions vary over a range of about 1-80. Substitution appears to be homogeneous, and it is reasonable to suppose that the Mn(IV) is substituted for Sn(IV) in K_2SnCl_6. Crystals of K_2SnCl_6 are cubic and belong to space group *Fm*3*m* (O_h^5).[11] Tin, and consequently manganese, is surrounded by six chlorines in a regular octahedral array. K_2SnCl_6 has, however, recently been shown by nuclear quadrupole resonance spectroscopy to undergo phase transitions at 260 and 264.5°K.[12] Since the interpretation of the optical data depends on the assumption that the manganese environment is octahedral near 77°K, we investigated the temperature dependence of the esr spectrum of $K_2Sn(Mn)Cl_6$ to determine if these phase transitions affect the manganese environment.

Table I. Esr Data for $K_2Sn(Mn^{II})Cl_6$

Temp, °K	*g*	$\langle a\rangle$,[a] G	Preparative method
290	2.005	70.7	2
290	2.005	71.3	1
250	2.006	70.4	2
170	2.006	70.9	2
100	2.005	70.8	2

[a] Values ±0.5 G.

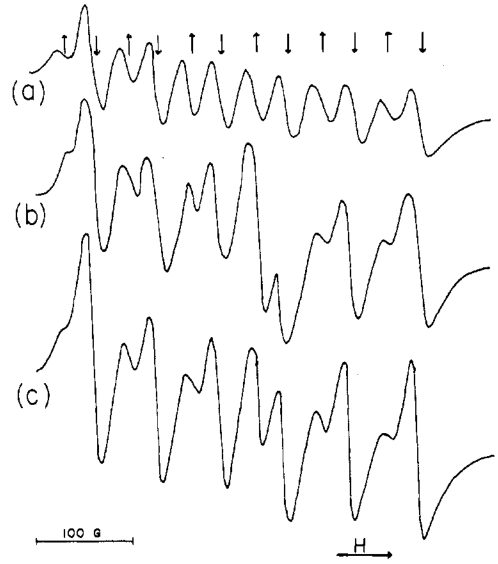

Figure 1. Esr spectra of $K_2Sn(Mn)Cl_6$ (polycrystalline): (a) at 110°K; (b) sample (a) at 110°K after being heated to 450°K for 30 min; (c) sample (a) at 110°K after being heated to 450°K for 60 min. ↑ indicates lines due to Mn(IV); ↓ indicates lines due to Mn(II).

The esr spectrum of polycrystalline $K_2Sn(Mn)Cl_6$ at room temperature consists of six lines representing a hyperfine splitting constant of 70.5 G and a $\langle g\rangle$ value of 2.0060. When this polycrystalline sample was cooled and esr spectra were recorded at 10° intervals between 290 and 100°K, the set of lines observed at room temperature remained unchanged (see Table I). This indicates that if these samples of $K_2Sn(Mn)Cl_6$ do in fact undergo the same phase transitions as pure K_2SnCl_6, the Mn environment remains octahedral, as it is at room temperature.

More interesting, however, was the observation of a second set of six lines at lower temperature representing a splitting constant of 73.9 G and a $\langle g\rangle$ value of 2.0307. This set of lines appeared gradually and reversibly between 110 and 300°K provided the crystals were not subjected to prolonged storage or heating between the measurements. Various preparations of $K_2Sn(Mn)Cl_6$ showed various ratios of these two sets of lines at the same temperature (110°K). A typical dual spectrum is shown in Figure 1a at 110°K.

The identity of these two sets of lines can be resolved quite easily. It is known that the $MnCl_6^{2-}$ species is sensitive to reduction (by chloride?) to lower oxidation states.[9] When a sample which showed both sets of lines was warmed to 450°K for 30 min and then the esr spectrum was recorded

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(11) R. W. G. Wycoff, "Crystal Structures," Vol 3, 2nd ed, Interscience, New York, N. Y., 1965, p 342.

(12) A. Sasane, D. Nakamura, and M. Kubo, *J. Magn. Resonance*, 3, 76 (1970).

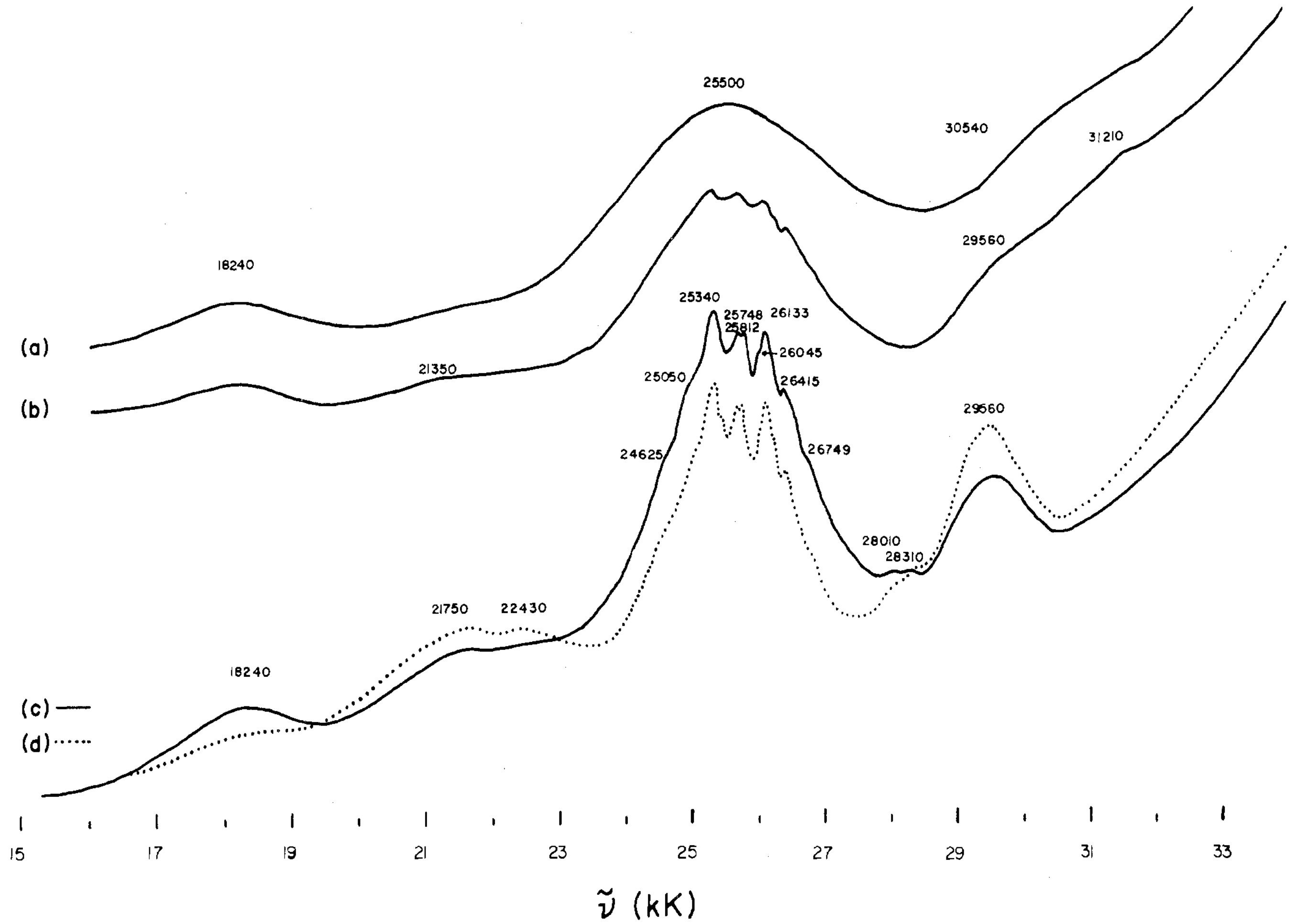

Figure 2. Crystal spectra of $K_2Sn(Mn)Cl_6$ at 77°K from 15 to 33 kK: (a) crystal prepared by method 1; (b) crystal prepared by method 2; (c) crystal prepared by method 3; (d) same as crystal (c) after standing in dark for 3 years. All intensities are relative. At 77°K K_2SnCl_6 itself begins to absorb weakly at about 500 nm (20 kK) and provides a continuously rising background ($I \leqslant \sim 0.5$) to ~300 nm (~33 kK). Around 280 nm (~35 kK) it begins to absorb so strongly as to completely obscure the absorption of any substituents beyond this point.

again at 110°K, the set of lines observed at room temperature became more intense (Figure 1b). Thus, this set observed at 300°K represents Mn(II) [d^5] ($g = 2.0060$), and the other set observed only at lower temperatures represents Mn(IV) [d^3] ($g = 2.0307$). Since all optical transitions of Mn(II) are spin forbidden, Mn(II) might not be detectable by optical means, even though its absolute concentration could be fairly high.

Optical Spectrum of $MnCl_6^{2-}$. Jezowska-Trzebiatowska and coworkers[10] have found that the absorption spectrum of K_2MnCl_6 in 12 *M* HCl shows three bands at 17.0, 25.0, and 43.5 kK, the first two having relative intensities of about 1:5. They assigned the first two bands to the lowest spin-allowed d-d transitions in $MnCl_6^{2-}$ (d^3), ${}^4A_2 \rightarrow {}^4T_2$ and ${}^4A_2 \rightarrow {}^4T_1$ (F), and the third band to a charge-transfer process. The third d-d transition, ${}^4A_2(t_{2g}{}^2) \rightarrow {}^4T_1(e_g{}^2)$ (P), which involves two electrons, was not observed. Since this transition is expected to be weak and is calculated to appear around 39 kK (see below), presumably it is masked by the very strong charge-transfer transition. The crystal spectrum of $K_2Sn(Mn^{IV})Cl_6$ (Figure 2a) shows the first two of these bands at 18,240 and 25,500 cm^{-1}. They are unstructured at 77°K and at this temperature are at somewhat higher energy than the bands observed in solution.[10] The spectra of various crystals, however, show other weak bands and interesting spectral features which must be explained. Most noticeable are weak broad bands at 12,020, 21,750, 22,430, 29,560, 31,210, and 34,930 cm^{-1} (not shown here), as well as fine structure on the 25,500-cm^{-1} band. The crystal whose spectrum is shown in Figure 2a was prepared according to method 1, while the one whose spectrum is shown in Figure 2b was prepared by method 2.

The value of $10Dq$ for $MnCl_6^{2-}$ can be approximated by use of the equation of Jorgensen[13] $10Dq$ (kK) = fg, where f and g are spectrochemical parameters for the ligand and the metal, respectively. Jorgensen estimated that $f = 0.80$ for six chlorine ligands and $g = 23.0$ for Mn(IV). This would make $10Dq$ for $MnCl_6^{2-}$ equal to 18.4 kK. Since the energy of the first d-d transition for a d^3 ion, ${}^4A_2 \rightarrow {}^4T_2$, is exactly $10Dq$ and since the optical spectrum shows a band at 18,240 cm^{-1}, it is quite reasonable to assume that this represents the ${}^4A_2 \rightarrow {}^4T_2$ transition and gives the value of $10Dq$.

If the value of $10Dq$ is known for $MnCl_6^{2-}$, the effective spin-orbit coupling constant (ζ) can be calculated from $\langle g \rangle$ as in

$$g = 2.0023 + 8\lambda_{\mathrm{eff}}/10Dq \qquad (1)$$

$$\zeta = 2S\lambda_{\mathrm{eff}} \qquad (2)$$

Using $g = 2.0307$ (for Mn^{4+}) and $10Dq = 18{,}240\ cm^{-1}$, λ_{eff} is calculated to be 64.8 cm^{-1} and $\zeta = 194.4\ cm^{-1}$. If we now assume that the Racah parameter, B, is lowered from the

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(13) C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Reading, Mass., 1962, p 113.

free-ion value of 1064 cm^{-1} proportionally as the spin-orbit coupling constant is lowered from the free-ion value of 355 cm^{-1},[14] B for the complex is 584 cm^{-1}. This value is very close to that estimated from the optical solution spectrum,[10] namely, 591 cm^{-1}. It is also lower than that found for the Cs_2MnF_6 complex (650 cm^{-1})[6], which is expected since the Mn-Cl band should be more covalent than the Mn-F band.

If a reasonable value of C is assumed, the positions expected for the other absorptions of $MnCl_6{}^{2-}$ can be calculated by diagonalizing the Tanabe-Sugano matrices for a d^3 ion without spin-orbit coupling.[15] These values are shown in Table II.

All the optical spectral features are not due to Mn(IV). This is inferred from the fact that different preparations yield somewhat different spectra, and the spectra change as the crystals age (see Figure 2c, d) or if they are subjected to prolonged heating. While the esr spectra show that heating of the crystals increases the concentration of Mn(II) while reducing that of Mn(IV), no optical features in these crystals are ascribable to Mn(II). The weakest band in the spectrum of $MnCl_6{}^{2-}$ has an extinction coefficient of ~500,[10] while the strongest absorption in octahedral Mn(II) complexes in the range 18-35 kK has ϵ ~0.02-0.2.[16] Therefore, it can be readily calculated that all Mn(II) absorptions in the crystals studied here are below the limit of detection with the spectrophotometer used. Accordingly, the spectra can best be interpreted as a mixture of the spectra of Mn(IV) and Mn(III).

Let us discuss each of the bands in some detail, starting with the more certain.

(1) 18.2 kK. This decreases in size as the crystals age (Figure 2c, d) and also if they are heated. From the evidence above it can convincingly be ascribed to the ${}^4A_2 \to {}^4T_2$ transition in Mn(IV). It does not completely disappear, however, even after the crystal is heated for 96 hr at 100°. It may then lie over an absorption of Mn(III).

It is interesting to note that this band in $MnCl_6{}^{2-}$ shows no structure at 77°K. The corresponding band in Cs_2MnF_6 shows a progression of eight or nine members in 500 ± 15 cm^{-1} [6] or 490 cm^{-1}.[3] Reisfeld, *et al.*,[6] assumed that this is a progression in ν_1, which in the Raman spectrum has a value of 592 cm^{-1}.[3] Flint[3] pointed out that this could be a progression in ν_2 (Raman active, e_g symmetry, 508 cm^{-1}) which would indicate that $MnF_6{}^{2-}$ is tetragonally distorted in the ${}^4T_{2g}$ state. Such a dynamic tetragonal distortion has been observed for V^{2+} in MgO, also a d^3 ion in an O_h site.[17] If such a distortion is rendered impossible by the nature of the lattice, as appears to be the case in $K_2Sn(Mn)Cl_6$, no vibrational progression in ν_2 would be expected. This might explain the lack of any vibrational progression in the ${}^4A_2 \to {}^4T_2$ band in the chloro complex and be an added argument for the progression in Cs_2MnF_6 being one in ν_2 rather than in ν_1. The emission spectrum of Cs_2MnF_6 shows a broad band at *ca.* 13.0 kK due to ${}^4T_{2g} \to {}^4A_{2g}$ fluorescence. Its large Stokes shift and lack of a mirror-image relationship between emission and absorption was interpreted by Flint[3] to be a further suggestion that the ${}^4T_{2g}$ state in $MnF_6{}^{2-}$ does not have O_h symmetry.

Table II. Energy States for Mn(IV) in K_2SnCl_6

Level	Obsd, cm^{-1} (77°K)	Calcd,[a] cm^{-1}
${}^4A_2 \to {}^2E$		11,760
	12,020	
$\to {}^2T_1$		12,255
$\to {}^2T_2$		18,160
$\to {}^4T_2$	18,240	18,240
$\to {}^4T_1$	25,500	24,363
$\to {}^2A_1$		27,934
$\to {}^2T_2$		29,863
$\to {}^2T_1$		30,130
	31,200 (?)	
$\to {}^2E$		31,492
$\to {}^2T_1$		34,405
$\to {}^4T_1$		39,117

[a] $10Dq = 18{,}240$ cm^{-1}, $B = 584$ cm^{-1}, $C = 2453$ cm^{-1}, $\gamma = 4.20$.

(2) 24-27 kK. This band shows no structure at 77°K in crystals which *also* show no absorption at 29.5 kK. In another crystal in which the structure on the large band was poorly resolved at 77°K the 29.5-kK band was weak. Well-resolved structure on the lower energy band is accompanied by a strong band at 29.5 kK. The 25-27-kK band belongs to Mn(IV) and is clearly overlaid by another absorption, presumably of Mn(III). This band also decreases sharply in size with heating without, however, the destruction of the fine structure. As noted above, it has been assigned to the second d-d transition in $MnCl_6{}^{2-}$,[10] and calculations indicate that this transition should occur at about 24.3 kK. In an ion in a 4+ oxidation state large covalency and some charge transfer are expected. This would make the electronic transitions more allowed and help account for the high intensity of this band.

The structure that grows in then appears to be due to Mn(III). The structure is fairly well resolved at 77°K and seems to consist of two overlapping progressions of about 305-315 cm^{-1}. The ir spectrum of $(Co(pn)_3)(MnCl_6)$ (pn = 1,2-propanediamine) shows bands at 183 and 342 cm^{-1};[18] these are probably the t_{1u} normal modes ν_4 and ν_3. The Raman-active symmetric stretch (ν_1, a_{1g}) is, in most cases, of similar magnitude to ν_3[19] and often in the excited state is smaller than in the ground state. Therefore, it is quite probable that the progressions observed here are in ν_1. A discussion of the possible nature of this Mn(III) transition will be found below.

(3) 12.0 kK. In the spectra of the most concentrated crystals there is a weak, broad, and probably multiple absorption centered at ~12.0 kK. Its intensity relative to the 18.2-kK band varies in different crystals; it is at most about 8% as intense as the latter and in some crystals less than 2%. Calculations (Table II) indicate that the ${}^4A_2 \to {}^2E$, ${}^2T_1$ transitions in Mn(IV) should appear in this range. Furthermore, many high-spin Mn(III) complexes have a band of somewhat uncertain origin in this region.[20,21] When rather highly substituted crystals are irradiated with light of 320 nm for 10 min, the contour of this band changes somewhat. The instability of Mn(III) complexes toward photodecomposition has been noted.[20,21] When the crystals are heated for varying periods of time the band *seems* to become less intense. But this latter effect is not clear because of the varying background, the crystals becoming less transparent with heating. The situation is complicated by the weakness of the band and the fact that the visible and ir detectors in the

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(14) T. M. Dunn, *Trans. Faraday Soc.*, **57**, 1441 (1961).

(15) See, *e.g.*, R. Stevenson, "Multiplet Structure of Atoms and Molecules," W. B. Saunders, Philadelphia, Pa., 1965, p 165 ff.

(16) N. S. Hush and R. J. M. Hobbs, *Progr. Inorg. Chem.*, **10**, 327 (1968).

(17) M. D. Sturge, *Phys. Rev. A*, 140, 880 (1965).

(18) D. M. Adams and D. M. Morris, *J. Chem. Soc. A*, 694 (1968).

(19) D. M. Adams, "Metal-Ligand and Related Vibrations," St. Martin's Press, New York, N. Y., 1968, p 62 ff.

(20) R. Dingle, *Acta Chem. Scand.*, **20**, 33 (1966).

(21) T. S. Davis, J. P. Fackler, and M. J. Weeks, *Inorg. Chem.*, **7**, 1994 (1968).

Table III. Spectroscopic Data for Some High-Spin Mn(III) Complexes

Compd	Method	Bands				Ref
$(Co(pn)_3)(MnCl_6)^a$	Reflt	8,333	17,540		22,400	*b*
$(Rh(pn)_3)(MnCl_6)^a$	*c*		17,540		22,400	*d*
$K_2Sn(Mn^{III})Cl_6$	Transmission, 77°K	12,020	18,240	21,750 + 22,430	~25,500	*e*
K_2MnCl_5	Reflt	12,000	18,500			*b*
$(Et_4N)_2In(Mn)Cl_5$	Transmission	11,500 (*xy, z*)	~15,000 (*xy*)	16,000 (*xy*)	23,900 (*xy*)	*b*
$(Et_4N)_2MnCl_5$	Reflt, 77°K	11,300	16,200		23,530	*b*
$(bipyH_2)MnCl_5{}^g$	Reflt	11,500	17,240		24,400	*h*
$(bipyH_2)MnCl_5{}^g$	Transmission	13,700 (*xy, z*)	16,900 (*xy*)	18,200 (*z*)	23,900 (*xy,z*)	*f*
$(phenH_2)MnCl_5{}^i$	Reflt	12,500	17,400		~25,000	*h*
$(phenH_2)MnCl_5{}^i$	Transmission	14,000	17,500		24,000	*f*

[a] pn = 1,2-propanediamine. [b] Reference 21. [c] Pressing in CsCl at 77°K. [d] W. E. Hatfield, R. C. Fay, C. E. Pfluger, and T. S. Piper, *J. Amer. Chem. Soc.*, **85**, 265 (1963). [e] This work. [f] Reference 24. [g] $bipyH_2$ = bipyridinium ion. [h] H. A. Goodwin and R. N. Sylva, *Aust. J. Chem.*, **18**, 1743 (1965). [i] $phenH_2$ = phenanthrolinium ion.

Cary 14 are both least efficient in this region. The band is probably an overlay of absorptions of both Mn(III) and Mn(IV).

Beyond these three bands, no other absorption can unambiguously be assigned to Mn(IV), and it seems that most of the remaining features can be ascribed to Mn(III).

Optical Spectrum of Mn(III). Mn(III) (d^4) can exist as either a high-spin or a low-spin ion. While six chloride ligands are expected to produce only a moderate ligand field and leave Mn(III) in the high-spin state, they could conceivably induce spin pairing if the lattice parameters indicated a significant contraction of the normal Mn^{3+} ion size. In K_2SnCl_6 the Sn-Cl distance is 2.45 Å.[11] If the Cl^- ion radius is assumed to be 1.81 Å,[22] the Sn^{4+} radius would be 0.64 Å. Mn^{3+} in six-coordinate complexes has a radius of 0.65 Å (high spin) and 0.58 Å (low spin).[23] So on the basis of ion sizes there is no reason to postulate spin pairing in Mn(III). Furthermore, even when one chooses reasonable values of *B, C,* and *Dq* which would induce spin pairing, no correlation between calculated values and the observed spectrum can be made. The spectrum should accordingly be interpreted as due to some high-spin Mn(III) species.

High-spin Mn(III) is expected to be subject to large Jahn-Teller distortion. The single spin-allowed d-d transition thus becomes multiple as Figure 3 shows. Davis, Fackler, and Weeks[21] have calculated that a reasonable splitting of the ^5E_g level in Mn(III) due to Jahn-Teller distortion is 8000 cm^{-1} or more and noted that the splitting in the $^5T_{2g}$ level should be less, since it is composed of the electron configuration $t_{2g}{}^2e_g{}^2$. Many solution and transmission mull spectra for Mn(III) complexes together with assignments based on the energy level diagram shown in Figure 3 have been reported.[21] (See Table III.)

More recently Bellitto, Tomlinson, and Furlani[24] have reported polarized crystal spectra of $(Et_4N)_2In(Mn^{III})Cl_5$ and $(bipyH_2)MnCl_5$ ($bipyH_2$ = bipyridinium ion). The principal difference between these groups in their assignments for the $MnCl_5{}^{2-}$ ion is that of the most intense band at ~24 kK. It is assigned to a charge-transfer process by Bellitto, *et al.*,[24] who observed three weaker absorptions between 10 and 20 kK which could be assigned to the three expected d-d transitions. The mull and solution spectra of Davis, *et al.*,[21] showed only two bands in this region and they accordingly assigned the band at ~24 kK to the third d-d transition.

The former interpretation appears more reasonable and can be applied to the Mn(III) spectrum in K_2SnCl_6. If the reduction of Mn(IV) by an electron from Cl^- leaves the chlorine atom *in situ*, the remaining manganese species would be the tetragonal-pyramidal $MnCl_5{}^{2-}$ (C_{4v} symmetry). (It is also possible that nearby Cl atoms might migrate and form molecular Cl_2 in the lattice.) The bands to be assigned are the weak absorptions at 12.0, 18.2, and 22 kK, the structured band at ~25 kK, and that at 29.5 kK. In the spectra of some crystals, especially those which have stood a long time, the band around 22 kK shows two principal peaks. The lower (21.7 kK) is found in all crystals that have been heated. The upper (22.4 kK) grows in as the crystal ages. The band at 29.5 kK also grows in as the crystals age. In some spectra this latter band shows some poorly resolved fine structure whose spacings cannot be accurately determined. After prolonged heating it does not disappear but remains of comparable intensity with the other bands.

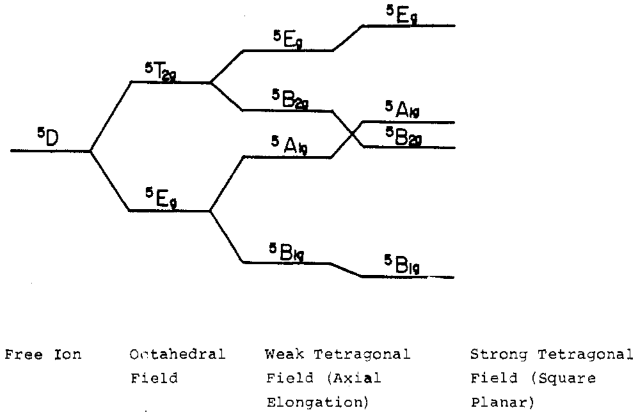

Figure 3. Tetragonal splitting diagram for ^5D (d^4) (from ref 21).

Accordingly, a probable assignment of the d-d spectrum of the $MnCl_5{}^{2-}$ species is as follows: $^5B_1 \rightarrow {}^5A_1$, 12.0 kK; $^5B_1 \rightarrow {}^5B_2$, 18.2 kK; $^5B_1 \rightarrow {}^5E$, 21.7, 22.4 kK. Our data should be more like those reported for $MnCl_5{}^{2-}$ than for $MnCl_6{}^{3-}$. The data in Table III indicate that this is in fact so. If the symmetry of the chromophore is reduced from C_{4v} to C_{2v} the last band would split into two. This could be the reason for the double band (21.7, 22.4 kK) which is observed most clearly in the crystal which aged 3 years.

The more intense bands above 23 kK may then be ascribed to charge-transfer processes. This leaves, however, the anomaly of the lowest charge-transfer band in Mn(III) being lower in energy than that in Mn(IV). While this is certainly not expected according to the usual order found for octahedral complexes,[25] we must remember that we are not dealing here with two complexes of O_h symmetry and so simple comparisons may be untrustworthy.

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The very weak bands in the spectrum at 28.1 and 28.3 kK do not appear to change intensity much as the crystal ages. They may be due to some spin-forbidden process, but this cannot at present be further specified. Likewise the nature of the weak shoulders above 31 kK cannot at present be determined.

Registry No. K_2SnCl_6, 16923-42-5; K_2MnCl_6, 16923-41-4.

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Reactions of the $W(CO)_5Cl^-$ Anion with WCl_6

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The reaction of $W(CO)_5Cl^-$, WCl_6, and Cl^- was examined in CH_2Cl_2 solution with the hope that $W_2Cl_9^{3-}$ could be synthesized according to $W(CO)_5Cl^- + WCl_6 + 2Cl^- \rightarrow W_2Cl_9^{3-} + 5CO$. However, mixtures of other products were formed. Adjustment of the stoichiometry led to either WCl_6^{2-} or WCl_6^- depending on the $W(CO)_5Cl^-$:WCl_6 ratio. Polynuclear chlorotungstates, $W_2Cl_9^{2-}$ and $W_4Cl_{17}^{2-}$, along with $W(CO)_6$ and $WCl_4(CO)_2$ and/or $W(CO)_4Cl_3^-$, were formed only when Cl^- was not present initially. In tetrahydrofuran, however, $WCl_4(THF)_2$ and $W(CO)_4Cl_3^-$ were the products. The reaction of $W(CO)_6$ and WCl_6 was found to yield W_2Cl_9O.

Although polynuclear halometalates are generally formed by nature's wish rather than by man's design, we have recently attempted to develop a more rational synthesis of the $W_2Cl_9^{3-}$ anion. Originally prepared by the reduction of W(VI) in aqueous hydrochloric acid solution,[1] this anion has been synthesized according to several similar but modified procedures,[2,3] including one from this laboratory.[4] The reaction, which is by no means well understood, apparently proceeds by way of the one-electron reduction product $WOCl_5^{2-}$, followed by a two-electron reduction to $W_2Cl_9^{3-}$.[5] The involvement of $Cl_5WOWCl_5^{4-}$, recently proposed to be a W(III)-W(V) mixed-valence ion, has been discussed by Konig.[6,7]

An alternate route, which we hoped would lead rationally to the synthesis of this anion, uses the notion that WCl_6 can serve as an easily reduced tridentate ligand. The reducing agent, $W(CO)_5Cl^-$, was chosen because CO should be easily displaced under oxidative conditions. The planned reaction was then

$$W(CO)_5Cl^- + WCl_6 + 2Cl^- \rightarrow W_2Cl_9^{3-} + 5CO \qquad (1)$$

We envisioned that $W(CO)_5Cl^-$ would react with WCl_6 by stepwise facial displacement of CO, with concomitant electron transfer, to form a series of unstable intermediates that would terminate with $Cl_3WCl_3W(CO)_2Cl^-$. Displacement of CO from this anion should proceed smoothly due to the relatively high formal oxidation state of the tungsten atom to which this ligand is bound. Providing the solvent could not easily compete for these coordination sites, the reaction with Cl^- should lead to the desired product. However, the results of this experiment showed that man's design remained subservient to nature's wish.

Experimental Section

Reagents and Procedures. All solvents were of reagent grade quality and were dried prior to use by standard procedures. The alkylammonium halides were dried in a drying pistol over P_4O_{10} at 50°. Commercially available WCl_6 was purified by fractional sublimation (150°, 0.1 Torr) immediately before use. The method of Abel, *et al.*,[8] was used in the preparation of $[R_4N]W(CO)_5Cl$ ($R = C_2H_5$, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$).

Reactions were performed in evacuated, greaseless glass vessels connected to a vacuum line. The general procedure in those reactions in which CO was evolved was to allow the reaction to proceed until gas evolution ceased. The reaction mixture was then frozen with liquid nitrogen and CO was removed for measurement through a series of traps by a Toepler pump.

Reactions of $[(C_4H_9)_4N]W(CO)_5Cl$, WCl_6, and $[(C_4H_9)_4N]Cl$. 1:2:5. The addition of 25 ml of a CH_2Cl_2 solution of $[(C_4H_9)_4N]W(CO)_5Cl$ (0.45 mmol) and $[(C_4H_9)_4N]Cl$ (2.24 mmol) to solid WCl_6 (0.90 mmol) caused a vigorous evolution of CO. At the end of 1 hr, gas evolution had ceased and 95% of the available CO had evolved. The electronic spectrum of this solution indicated that the only chromophoric species present in solution was WCl_6^{2-} (1.3 mmol). An infrared spectrum of this solution indicated the absence of compounds containing CO. The product was isolated by adding ether until the yellow-green solution became cloudy and then cooling to −80°. The pastel green, microcrystalline solid was filtered off at −80° to prevent formation of an oil. After filtration, the solid was washed with the cold distillate from the mother liquor, allowed to warm to room temperature, and dried under vacuum. *Anal.* Calcd for $[(C_4H_9)_4N]_2WCl_6$: Cl, 24.2; W, 20.9. Found: Cl, 24.1; W, 21.4.

1:5:5. When $[(C_4H_9)_4N]W(CO)_5Cl$ (0.79 mmol) and $[(C_4H_9)_4N]Cl$ (3.92 mmol) in 25 ml of CH_2Cl_2 were added to solid WCl_6 (3.91 mmol), immediate evolution of CO occurred. Gas evolution appeared to cease after 15 min, but the solution was stirred for 1 additional hr to ensure complete reaction. At the end of that time, it was found that 96% of the available CO had evolved. One milliliter of solution was taken by syringe and diluted to 5 ml. The electronic spectrum indicated that the only chromophoric species present in solution was WCl_6^-. Large orange platelets of $[(C_4H_9)_4N]WCl_6$ were obtained by the addition of ether. The elemental analysis indicated a small quantity of some impurity. Recrystallization did not remove the

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