

**687.** *Structure and Reactivity of the Oxyanions of Transition Metals. Part XIII.\* The Effect of Environment and Certain Complex-forming Cations on the Visible and Ultraviolet Absorption Spectra of Permanganate and Chromate.*

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Small differences in the energy of the first electronic absorption band for permanganate in different solvents and on change of temperature are discussed in terms of the nature of the transition, and are related to the larger shifts observed by Teltow for permanganate in different host crystals. The possible significance of these results in the theory of ionic solvation is stressed. The effect of "contact" ion-pair formation in solvents of low dielectric constant on the absorption spectrum is considered, and is contrasted with the effect to be expected if a complex ion is formed. Spectral evidence for complex-formation between silver ions and permanganate or chromate is presented and the spectra of such complexes are discussed.

COMMONLY, electronic transitions are somewhat modified by the environment of the absorbing species, with resulting changes in the maxima, widths, intensities, or fine structure of the spectral profiles. If the nature of the electronic transition is known, at least in a general sense, a study of these changes can give valuable information about the nature of the interactions involved.<sup>1, 2</sup>

The electronic spectra of "closed-shell" oxyions of transition metals are remarkably insensitive to changes in environment. This contrasts with the extreme susceptibility of the ultraviolet spectrum of halide ions to environmental changes<sup>3</sup> and has been invoked in support of the concept that, for the latter, the solvent plays a dominant role in determining the nature of the excited state.<sup>4</sup> The systems are comparable in that anions are

\* "Advances in the Chemistry of the Coordination Compounds," Macmillan, New York, 1961, p. 430, is considered as Part XII; Part XI, *J.*, 1961, 3204.

<sup>1</sup> Kosower, *J. Amer. Chem. Soc.*, 1958, **80**, 3253, 3261; Bayliss, *J. Chem. Phys.*, 1950, **18**, 292; Sidman, *Chem. Rev.*, 1958, **58**, 689; Brealey and Kasha, *J. Amer. Chem. Soc.*, 1955, **77**, 4462.

<sup>2</sup> Smith and Boston, *J. Chem. Phys.*, 1961, **34**, 1396.

<sup>3</sup> Smith and Symons, *Discuss. Faraday Soc.*, 1957, **24**, 206.

<sup>4</sup> Smith and Symons, *Trans. Faraday Soc.*, 1958, **54**, 338, 346; Stein and Treinin, *ibid.*, 1959, **55**, 1086, 1091.

involved and the charge distribution is centrosymmetric for ground and excited states. However, for the oxyions under consideration, there is a movement of charge inwards in the first excitation process, whereas there is a corresponding outward movement for the first transition of solvated halide ions.

TABLE 1.

Details of the visible spectrum of permanganate in various solvents.

Salt	Solvent	$\lambda_{\max}$ ( $m\mu$ ) *	Temp. (K)	Ref.	Salt	Solvent	$\lambda_{\max}$ ( $m\mu$ ) *	Temp. (K)	Ref.
†	H <sub>2</sub> O	525.6	273°	6	KMnO <sub>4</sub>	MeOH ‡	528.5	273°	6
†	"	525.0	—	a	"	"	529.5	289	b
†	"	526.5	289	b	"	EtOH ‡	528.2	273	6
KMnO <sub>4</sub>	Me <sub>2</sub> CO ‡	527.6	273	6	"	MeCN ‡	525.8	273	6
"	"	530.0	289	b	"	"	526.5	289	b
Ph <sub>4</sub> AsMnO <sub>4</sub>	"	528.0	289	b	"	H·CO·NMe <sub>2</sub> ‡	529.0	289	b
					Ph <sub>4</sub> AsMnO <sub>4</sub>	CHCl <sub>3</sub> ‡	528.0	289	b
					KMnO <sub>4</sub>	NH <sub>3</sub>	527.0	240	c

$\Delta\nu \approx 750 \text{ cm}^{-1}$  in all cases and judged from the resolved bands in 526 and 548  $m\mu$  region.

\* The most prominent band in the spectrum. † Wide range of common salts. ‡ Solutions decomposed, giving initially colloidal MnO<sub>2</sub>. Refs.: (a) Hagenbach and Percy, *Helv. Chim. Acta*, 1922, 5, 454; (b) this work; (c) Jolly, U.C.R.L., 1952, No. 2008.

Teltow,<sup>5</sup> who studied the spectra of single crystals containing permanganate in low concentration (Fig. 1), and Merton,<sup>6</sup> who studied the effect of varying the solvent (Table 1), showed that shifts can be detected, although they are very small. One purpose of this paper is to extend Merton's work and to consider possible interpretations.

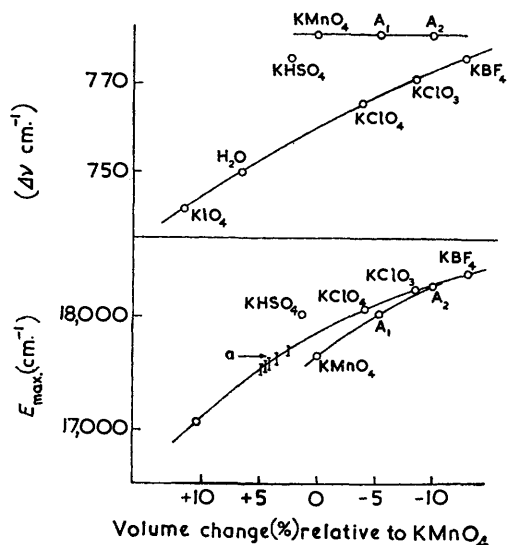


FIG. 1. Effect of environment on spectrum of permanganate.

A<sub>1</sub> and A<sub>2</sub>: KMnO<sub>4</sub> under pressure, from data of Bentley and Drickamer.<sup>14</sup> (a) 200  $\text{cm}^{-1}$  added to values at 289° K from Table 1 for purpose of comparison.

Few complex ions having transition-metal oxyions as ligands have been studied spectrophotometrically. Tong and King<sup>7</sup> detected interaction between trivalent and hexivalent chromium, and studied by measurements at suitable wavelengths, but they did not report the overall spectrum of the complex. Teltow<sup>5</sup> found that the visible spectrum of silver permanganate and of dilute "solutions" of permanganate in the monohydrate of silver perchlorate differed markedly from those of alkali-metal salts, and discussed this in terms of the formation of manganate.

<sup>5</sup> Teltow, *Z. phys. Chem.*, 1938, B, 40, 397; 1939, B, 43, 198.

<sup>6</sup> Merton, *J.*, 1911, 99, 637.

<sup>7</sup> Tong and King, *J. Amer. Chem. Soc.*, 1953, 75, 6180.

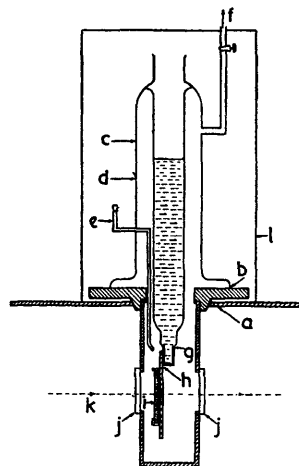
One possible description of such complexes includes a  $\sigma$ -bond to the cation using non-bonding electrons on one of the oxygens of the anion. Such a complex would then have local  $C_{3v}$  symmetry with respect to the metal of the oxyion, and, as with comparable proton<sup>8</sup> and alkyl derivatives,<sup>9</sup> a characteristic change in the spectrum of the oxyion would be expected. With this in mind, we have measured the spectrum of permanganate and chromate ions in solutions containing cations which might be expected to interact in this way.

#### EXPERIMENTAL AND RESULTS

**Materials.**—Silver permanganate, prepared from aqueous silver nitrate, was recrystallised from water, dried *in vacuo*, and stored in the dark. Tetraphenylarsonium permanganate was precipitated from an aqueous solution of the chloride by addition of aqueous potassium permanganate and dried *in vacuo* after being washed with hot water. Silver chromate adsorbed on silver chloride was prepared by adding a slight excess of aqueous silver nitrate to a solution of potassium chloride containing a trace of potassium chromate. The precipitate was dried and stored *in vacuo* in the absence of light.

FIG. 2. Low-temperature cell for Unicam S.P. 700 spectrophotometer.

- (a) Spare lid from S.P. 700, locating brass flange and "S" band rectangular waveguide. (b) "Araldite" seal to glass flange, forming vacuum-joint. (c) Removable glass vessel for coolant. (d) B44 joint. (e) Liquid  $N_2$  inlet for initial cooling; stoppered after operation. (f) Vacuum-system. (g) Glass-to-copper seal. (h) Copper cell-holder soldered to g. (i) 1 mm. quartz cell containing sample. (j) Quartz windows, sealed with "Araldite." (k) Light path. (l) Metal cover as light shield.



Water was doubly distilled from alkaline permanganate. Other solvents were "Spectrograde" materials, dried over calcium hydride.

**Ultraviolet and Visible Spectra.**—Spectra of solutions were measured as soon as possible after preparation by using Unicam S.P. 600 and S.P. 700 spectrophotometers. The spectrum of permanganate in saturated aqueous silver perchlorate at 77° K, under which conditions a good glass was obtained, was measured with the S.P. 700 instrument and a modified cell-holder depicted in Fig. 2.

Reflectance spectra were obtained by appropriate dilution of the powdered salt with lithium fluoride which was also used as a reference surface. Finely powdered mixed crystals grown from aqueous solutions by slow evaporation in a desiccator did not require further dilution, and the parent salt was used as reference. Normal precautions were observed.<sup>10</sup> Spectra from powders at 77° K, which were far better resolved than those from powders at room temperature, were obtained by using the Unicam S.P. 540 attachment equipped with a modified sample tray.<sup>11</sup>

Transmission spectra of pressed discs were measured with the S.P. 700 instrument. Those for permanganate in potassium chloride were better resolved than those obtained by reflectance methods (Table 2). However, in most other instances very poor spectra were obtained. Discs were prepared from carefully dried salts powdered in a ball mill. A pure potassium chloride

<sup>8</sup> Bailey, Carrington, Lott, and Symons, *J.*, 1960, 290.

<sup>9</sup> Klänning and Symons, *J.*, 1961, 3204.

<sup>10</sup> Griffiths, Lott, and Symons, *Analyt. Chem.*, 1959, **31**, 1338.

<sup>11</sup> Symons and Trevalion, *Spectrovision*, 1961, **10**, 8.

disc was used in the reference beam of the spectrometer, and, if the optical density of the sample was too high, a matt-black 40-mesh gauge was also employed.

*Results.*—The addition of a large excess of a saturated aqueous solution of ferrous, mercuric, or aluminium nitrate, of cadmium sulphate, or of mercuric or zinc perchlorate had no detectable effect on the spectrum of aqueous permanganate.

Quantitative estimation of equilibrium constants for the formation of silver complexes was not attempted since the solutions were unstable. For solutions of silver permanganate in aqueous silver perchlorate it was necessary to extrapolate spectral readings to "zero time" since colloidal manganese dioxide gives rise to an apparent shift of the visible band to higher energies.

TABLE 2.  
Spectra of  $\text{KMnO}_4$  in different environments.

Environment	Temp. ( $\kappa$ )	$\Delta\nu$ ( $\text{cm.}^{-1}$ )		Spectral details ( $m\mu$ )					
KBr disc .....	289°	766	568	545	524	502	484	467	450
$\text{KMnO}_4$ powder * .....	289	750	568	545	525	505	485		
$\text{KClO}_4$ powder * .....	289	750	558	535	515	495	478	461	446
„ * .....	77	766	554	530	510	490	473	456	441
„ † .....	20	764	554	531	511	492	474	456	442

\* Diffuse reflectance, dilution with LiF if necessary. † Results reported by Teltow,<sup>5</sup> averaged for three directions.

TABLE 3.  
Spectra of silver permanganate in different environments.

Environment	Temp. ( $\kappa$ )	Spectral details ( $m\mu$ )								Species
$\text{H}_2\text{O, MeCN}$ .....	289°	Normal spectrum for $\text{MnO}_4^-$								$\text{MnO}_4^-$
KCl disc * .....	289	" "								"
$\text{AgMnO}_4$ powder † .....	289	570 †								$\text{AgMnO}_4$
Sat. aqueous $\text{AgClO}_4$	289	577 † weaker band at 400								"
„ „	77									"
$\text{AgClO}_4$ powder † .....	289	590 † shoulders 555, 535								"
„ „	77	600 §	575	552	530	510	490	475	458	"
$\text{AgClO}_4$ crystal    .....	20	600 ¶	575	552	530	510	492	474	458	"

\* Double decomposition. † Diffuse reflectance, dilution with LiF if necessary. ‡ Broad maximum, no fine structure. §  $\Delta\nu = 732 \text{ cm.}^{-1}$ . || Results reported by Teltow,<sup>5</sup> averaged for two directions. ¶  $\Delta\nu = 737 \text{ cm.}^{-1}$ .

The colour of permanganate in aqueous silver perchlorate changed from violet to blue on cooling to 77°  $\kappa$ . However, only a very slight shift to low energy was detected in the fairly broad maximum.

Reflectance spectra of mixed crystals of small quantities of permanganate in potassium perchlorate and in silver perchlorate monohydrate at 77°  $\kappa$  were very well resolved, and maxima for the seven major bands could be measured with considerable accuracy (Tables 2 and 3). The results are very close to those of Teltow<sup>5</sup> for permanganate in single crystals of these salts at 20°  $\kappa$ .

## DISCUSSION

*Effect of Environment.*—The trend in  $\lambda_{\text{max}}$  to lower energies as the "free volume" increases (Fig. 1) cannot be simply a consequence of a decrease in  $\nu_1$ , the frequency of the symmetrical breathing mode, either in the ground or the excited state, although Teltow's results show that  $\nu_1$  for excited permanganate falls steadily, and the work of Price *et al.*<sup>12</sup> suggests strongly that a similar fall in  $\nu_1$  for the ground-state ion is to be expected. We suggest that a very simple electrostatic explanation adequately accommodates all the results for tetrahedral oxyions. Since the  $t_1 \rightarrow e$  transition is accompanied by a symmetrical inward movement of negative charge from oxygen, one can picture the nearest-neighbour cations as holding back the electrons, more or less effectively, depending upon their proximity and size. Teltow's results show that, for a given cation as its average

<sup>12</sup> Price, Sherman, and Wilkinson, *Spectrochim. Acta*, 1960, **16**, 663.

distance from the anion increases, so there is a steady trend to lower energies for each component of the  $t_1 \rightarrow e$  transition. As predicted by this model, a similar trend is found with increase in temperature.

That  $v_1$  for the excited state should decrease as the "free volume" increases is a consequence of greater freedom for the ion to expand and is not so directly linked to the nature of the electronic transition.

Our analysis is based on the assumption that the major contribution to the shift comes from the nearest-neighbour cations. We should include the nearest shell of anions whose presence must to some extent counter the effect of the cations but it is unlikely that further refinement to include more distant ions would modify the treatment appreciably. This conclusion has also been drawn by Smith and Boston<sup>2</sup> in their discussion of the effect of changing the cation upon the  $n-\pi^*$  transition of nitrate in molten alkali nitrates. The situation with nitrate differs in that cations in the melt could either hinder or facilitate the transition depending on their location relative to nitrate. The shifts recorded leave little doubt that, as with polar solvents,<sup>13</sup> the cations cluster preferentially near the oxygen and avoid the nitrogen.

*Effect of Pressure.*—Bentley and Drickamer<sup>14</sup> have studied the  $t_1 \rightarrow e$  transitions of permanganate and chromate in their potassium salts as a function of pressure. They observed a shift to higher energies with increasing pressure, the effect being comparable for both salts and tending to level off at a pressure of 120 kilobars. From their results for potassium permanganate at room temperature, we estimate 18,400  $\text{cm}^{-1}$  for the  $O \rightarrow O$  transition, a value close to that for permanganate in potassium tetrafluoroborate at 20°.<sup>5</sup> Indeed, after allowance for the difference in temperature it seems that both Teltow's results,<sup>5</sup> and those of Bentley and Drickamer<sup>14</sup> tend to a value which represents a limit for permanganate surrounded by six potassium ions. Curiously, the expected increase in  $\Delta v$  with increased pressure was not observed. Teltow's results<sup>1</sup> show that  $\Delta v$  for pure potassium permanganate is anomalously high, being close to that for permanganate in potassium tetrafluoroborate. These two observations probably have a common explanation which may be seated in the fact that an isolated "molecular" treatment is not strictly valid for undiluted solids of this sort. The effect of external pressure on  $E_{\text{max}}$  for the  $t_1 \rightarrow e$  transition of permanganate has been indicated on Fig. 1, where values for the volume change are estimated approximately from typical compressibilities for a range of similar salts.

*Solvation.*—The very small changes in  $\lambda_{\text{max}}$  found for the first band in the spectrum of permanganate in various solvents are in accord with the above postulate. In our view it is particularly significant that the results, extrapolated approximately to a common temperature, show that the effect of solvents is closely similar to that of a crystal field. Most studies of this type involve electronic transitions which involve gain or loss of electric dipoles, in contrast with the one under consideration. This difference is of significance to the problem of solvation, since it suggests a differentiation between those solvent molecules or ions in direct contact with the anion, and those more distant. The latter, to a good approximation, will not modify the energy under Frank-Condon conditions since there is no effective change in the electric field as a result of a centrosymmetric transition. We have already inferred that for ionic crystals only neighbouring cations and anions are directly involved. If this is so, then the effect of the first layer of solvent molecules must resemble that of the first layer of cations and anions in their ability to "hold back" the non-bonding electrons on permanganate. This conclusion, that ions in solution can be compared profitably with those in crystals, whilst not being shared by all who discuss ionic solvation, has been invoked recently in a discussion of the solvation of halide ions.<sup>15</sup>

*Ion-pairing and Complex-formation.*—In view of the considerations given above, it is

<sup>13</sup> Katzin, *J. Chem. Phys.*, 1950, **18**, 789.

<sup>14</sup> Bentley and Drickamer, *J. Chem. Phys.*, 1961, **34**, 2200.

<sup>15</sup> Griffiths and Symons, *Trans. Faraday Soc.*, 1960, **56**, 1125.

most unlikely that ion-pair formation would modify appreciably the  $t_1 \rightarrow e$  transition of the oxyions of transition metals unless the ions were in direct contact. Our experience with halide ions is that such "contact" ion-pairs are not important constituents in dilute solutions in any but the most non-polar solvents, such as carbon tetrachloride.<sup>16</sup> Unfortunately all the permanganates studied, including tetraphenylarsonium permanganate, were insoluble in such solvents.

However, complex formation should modify the spectrum considerably, as does protonation,<sup>8</sup> but it proved a difficult task to find conditions for preparing complexes, since most were either insoluble or unstable in suitable solvents. However, clear evidence of complex formation was obtained for silver salts.

*Silver complexes.* Even in aqueous solution, silver forms a complex with permanganate (Table 3). The spectral change parallels that found for permanganate in solid silver perchlorate<sup>5</sup> (Table 3) but is not, at first sight, in accord with expectation for an ion with local  $C_{3v}$  symmetry.

Teltow<sup>5</sup> drew attention to the similarity between the visible spectrum of silver permanganate and that of simple salts of manganate. One could, in the limit, even formulate the salt as  $Ag^{2+}MnO_4^{2-}$  but, although the lower energy bands occur in comparable regions, this is not the case for subsequent bands and there is thus little justification for such a formulation. It is worthy of note that the free energy of the reaction  $Ag^+ + MnO_4^- \rightarrow Ag^{2+} + MnO_4^{2-}$  is not large, so that a band corresponding to an electron-transfer of this type might be expected at fairly low energies, and, furthermore, any such tendency will modify the "normal" transition of permanganate. Thus we expect to find three features. First there should be a new band, characteristic only of the complex, probably in the near-ultraviolet region. There is, in fact, a greatly enhanced absorption in the 400  $m\mu$  region for silver permanganate which may be due to direct electron transfer from silver. Secondly, the  $t_1 \rightarrow e$  transition should have given way to  $a_2 \rightarrow 5e$  and  $4e \rightarrow 5e$  transitions,<sup>9</sup> which can, to a crude approximation, be associated, respectively, with electron transfer from the three oxide ligands and the oxygen linked to silver. Thirdly, relative to monoprotanated or monoalkylated ions,<sup>9</sup> the latter transition will be greatly modified by the silver, the effect being a stabilisation of the excited state by  $\pi$ -donation of electrons from silver to oxygen.

There are thus two opposing effects with respect to the oxygen linked to silver. On the one hand, a  $\sigma$ -bond is formed with one of the oxygen lone-pairs; this should cause a shift of the  $4e \rightarrow 5e$  transition to higher energies.<sup>8</sup> On the other, there is back-donation of  $d\pi$ -electrons from silver towards oxygen. This should tend to favour an electron-transfer from this oxygen to the transition metal and hence shift the  $4e \rightarrow 5e$  transition back to lower energies.

We tentatively postulate, that the  $4e \rightarrow 5e$  transition has moved to energies lower even than those of the  $t_1 \rightarrow e$  band of the free (uncomplexed) ion. This results in a merging of the two transitions, so that the spectral features normally characteristic of an ion with  $C_{3v}$  symmetry are not observed.

We have analysed the experimental spectra by using these concepts, and our tentative assignments are given in Tables 3 and 4. The relatively low value for the "breathing" frequency for excited permanganate in silver perchlorate is presumably a direct result of bonding to silver, and it would be of interest to analyse the marked anisotropy in the spectrum. In contrast with the temperature-dependence of the spectra of free (uncomplexed) ions, that for silver permanganate is positive. In terms of the present analysis there are two competing effects and the results suggest that the loosening of the weak silver-oxygen interaction dominates.

The results for silver chromate complexes are less readily interpreted because the three species  $AgCrO_4^-$ ,  $Ag_2CrO_4$ , and  $AgHCrO_4$  are involved in different experiments. It is

<sup>16</sup> Griffiths and Symons, *Mol. Phys.*, 1960, **3**, 90

TABLE 4.  
Spectrum of chromate in different environments.

Salt	Environment	Temp. (K)	Spectral details (m $\mu$ )		Assignment
K <sub>2</sub> CrO <sub>4</sub>	Aqueous alkali	289°	373		CrO <sub>4</sub> <sup>2-</sup>
"	Aqueous acid	"	351	444	HCrO <sub>4</sub> <sup>-</sup>
"	K <sub>2</sub> CrO <sub>4</sub> powder *	"	380	~430 †	CrO <sub>4</sub> <sup>2-</sup>
Ag <sub>2</sub> CrO <sub>4</sub>	Aqueous acid	289	351	444	HCrO <sub>4</sub> <sup>-</sup>
"	Ag <sub>2</sub> SO <sub>4</sub> solidified melt	"	—	455	Ag <sub>2</sub> CrO <sub>4</sub>
"	Ag <sub>2</sub> SO <sub>4</sub> solidified melt *	"	360	455	"
"	"	77	360	455	"
"	Ag <sub>2</sub> solidified melt	289	—	455	"
"	Sat. aqueous AgClO <sub>4</sub>	"	370	476	AgHCrO <sub>4</sub> + HCrO <sub>4</sub> <sup>-</sup>
"	Precipitated on AgCl *	"	260	410	AgCrO <sub>4</sub> <sup>-</sup>
ZnCrO <sub>4</sub>	Aqueous acid	289	351	444	HCrO <sub>4</sub> <sup>-</sup>
"	ZrCrO <sub>4</sub> powder *	"	380	~430	CrO <sub>4</sub> <sup>2-</sup>
"	Sat. aqueous Zn(ClO <sub>4</sub> ) <sub>2</sub>	"	360	455	ZnHCrO <sub>4</sub> <sup>+</sup> + HCrO <sub>4</sub> <sup>-</sup>
HgCrO <sub>4</sub>	Aqueous acid	289	351	444	HCrO <sub>4</sub> <sup>-</sup>
"	HgCrO <sub>4</sub> powder *	"	—	~420 †	HgCrO <sub>4</sub>
"	Sat. aqueous Hg(NO <sub>3</sub> ) <sub>2</sub>	"	357	455	HgHCrO <sub>4</sub> <sup>+</sup> + HCrO <sub>4</sub> <sup>-</sup>

\* Diffuse reflectance, diluted with LiF if necessary. † Shoulder. ‡ Very broad maximum.

hard to predict spectra except for the first of these, and our assignments are very tentative. There is clear evidence for complex-formation between Ag<sup>+</sup> and HCrO<sub>4</sub><sup>-</sup>. Also diffuse-reflectance results suggest that there is strong interaction between mercuric ions and chromate in the solid salt, and also between zinc ions and chromate.

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