166. *Structure and Reactivity of the Oxyanions of Transition Metals. Part V.* Quadrivalent Manganese.*

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Blue solutions obtained by dissolution of manganese dioxide in hot, concentrated aqueous potassium hydroxide consist of equimolar quantities of quinquevalent and tervalent manganese.

In an analysis of the electronic structure of certain tetrahedral oxyions,[1-3] use was made of the molecular-orbital treatment for the ions MnO_4^- and CrO_4^{2-} given by Wolfsberg and Helmholz.[3] These ions are described in terms of a " closed-shell " structure, and it was suggested that reduction of such ions involved feeding of further electrons into the first excited level, referred to by these authors as $(3t_2)$.[3] This molecular orbital is triply degenerate: however, it seems that the electron spin resonance spectrum of manganate in potassium chromate [4] is best described in terms of a level, containing the unpaired electron, which is doubly degenerate, and a preliminary study of hypomanganate in sodium vanadate appears to confirm this result. The issue is further complicated by the fact that Klemm [5] has reported a value of 3·6—3·7 B.M. for the magnetic moment of potassium hypoferrate, K_3FeO_4. If the compound studied is indeed K_3FeO_4, then this result, which is close to the free-spin value of 3·87 B.M. expected for three unpaired electrons, must mean that the orbital is at least three-fold degenerate, since if it were a doublet only one unpaired electron would be detected.

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* Part IV, *J.*, 1957, 659.

[1] Carrington, Ingram, Schonland, and Symons, *J.*, 1956, 4710.

[2] Carrington, Schonland, and Symons, *ibid.*, 1957, 659.

[3] Wolfsberg and Helmholz, *J. Chem. Phys.*, 1952, **20**, 837.

[4] Carrington, Ingram, Schonland, and Symons, unpublished work.

[5] Klemm, *Angew. Chem.*, 1954, **66**, 468.

It is therefore important to obtain more information regarding this level, and accordingly one object of this research was to prepare and study oxyions having three electrons outside the " closed-shell " (for convenience we will refer to these as " outer " electrons).

A variety of syntheses have been attempted ineffectually: in this work, possible compounds containing quadrivalent manganese were studied, and although the original aim was not realised, the results bear on the general chemistry of oxyions.

Some complexes of quadrivalent manganese, *e.g.*, K_2MnCl_6,[6] are known, but little work appears to have been carried out on alkaline solutions of Mn^{IV}, though manganese dioxide dissolved in aqueous potassium hydroxide, under nitrogen, at 180° has been reported to yield manganate.[7]

EXPERIMENTAL AND RESULTS.

All reagents were " AnalaR," and water was doubly distilled from concentrated alkaline potassium permanganate. Hydrogen peroxide was the destabilised product supplied by Laporte Chemicals.

Preparative Procedure.—Preliminary work showed that prolonged heating of hypomanganate in concentrated potassium hydroxide solution, in Pyrex containers under nitrogen, gave intense blue-violet solutions before reduction to the characteristic red of tervalent manganese. In fused silica, solutions of hypomanganate were stable to heat, and it thus appears that impurities from the glass caused the reduction, as in the case of the reduction of Cr^V to Cr^{III}.[8] Reaction with oxygen re-formed hypomanganate reversibly. It was thought that the deep blue solutions observed might have contained monomeric quadrivalent manganese, and solutions for investigation were prepared by the following methods: (*a*) Known weights of pyrolusite (crude manganese dioxide) were added to potassium hydroxide–water mixtures under nitrogen, and the resulting mixture was heated by means of a luminous Bunsen flame until all the manganese dioxide had dissolved. (*b*) Known volumes of standardised potassium permanganate solution, containing potassium hydroxide, were reduced to manganese dioxide by addition of excess of hydrogen peroxide. This solution was then heated to destroy the excess of peroxide, and solid potassium hydroxide was added to the hot solution, in an atmosphere of nitrogen, until all the manganese dioxide had dissolved and the solution had become a clear blue. At room temperature the solutions set to clear glasses.

Analytical Procedure.—The net valency state of manganese in these solutions was determined by estimating the oxidising power of those containing a known amount of manganese. The melts were dissolved in an excess of potassium iodide solution, under nitrogen, and acidified, and the liberated iodine was titrated with sodium thiosulphate solution previously standardised against the potassium permanganate solutions used in experiment (*b*). A number of determinations gave a valency state of $4{\cdot}0 \pm 0{\cdot}15$.

Spectrophotometric Analysis.—Because of the difficulties encountered in measuring the absorption spectra of " glasses,"[8] a method was developed for measuring those of the fluid melts. The temperature was kept above the softening point of the melt by use of a cell-housing, for the spectrophotometer, constructed of polystyrene foam, which is an efficient heat insulator. Measurements were made on a Unicam S.P. 500 spectrophotometer, and the silica reaction tubes were employed directly as cells. To avoid errors that arise from the curvature of the surface of the tubes, a constant slit width was used. The spectrum in the wavelength region of interest was scanned without altering the position of the test solution, and in order to obtain correct values of the optical density, a procedure similar to that described previously[8] was employed.

Dissolution of pyrolusite [procedure (*a*) above] gave initially a green solution whose colour resembled that of manganate. The spectra of such solutions were not reproducible, but were qualitatively similar to that shown in Fig. 1, and do not resemble the spectrum of manganate.[9] On prolonged heating the solutions became deep blue. The spectrum (Fig. 2) is characterised by two bands centred at 480 and 670 mμ. Since it had been established that there was no overall oxidation or reduction at this stage, it was considered possible that the spectrum

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[6] Weinland and Dinkelacker, *Z. anorg. Chem.*, 1908, **60**, 173.

[7] Eliot and Storer, *Proc. Amer. Acad.*, 1859, **1**, 43.

[8] Bailey and Symons, *J.*, 1957, **203**.

[9] Carrington and Symons, *J.*, 1956, **3373**.

was that of a monomeric quadrivalent manganese species. However, hypomanganate has a single band in the visible region with a peak at 670 mμ,[9] and hexaco-ordinated tervalent manganese complexes generally have a single band in the 470 mμ region.[10, 11] Direct measurement of the spectrum of tervalent manganese in concentrated potassium hydroxide solution confirmed this result in showing a single band in the visible region with a peak at 465 mμ, which may tentatively be ascribed to the ion $Mn(OH)_6^{3-}$. Since the apparent valency state of manganese in the blue solutions was four, it seemed probable that the constituents were hypomanganate and tervalent manganese in equimolar quantities. In order to confirm this, and to establish that none of the manganese was present in the quadrivalent state, a quantitative study of the spectra was made. From the spectra of the blue solutions after suitable adjustment for the overlapping band effect, values for the apparent extinction coefficients ($\varepsilon_{max.}$) for the bands at 670 and 470 mμ were estimated to be 820 and 385 respectively. These values are based on the assumption that 50% of the manganese is present as hypomanganate (670 mμ) and 50% as tervalent manganese (470 mμ).

The extinction coefficient found for hypomanganate is very close to that of 840 estimated previously,[9] and was confirmed by reaction of the solutions with oxygen to convert all the manganese into hypomanganate and remeasurement of the spectrum. The results were identical with those previously recorded.[9]

FIG. 1. *Absorption spectrum of solutions of manganese dioxide in potassium hydroxide formed initially (green).*

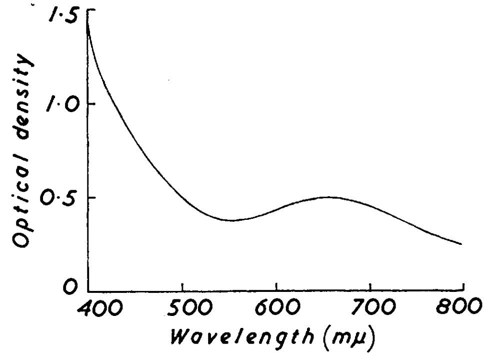
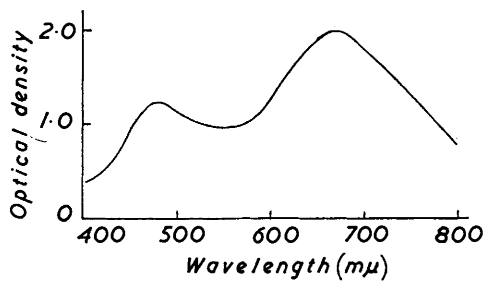


FIG. 2. *Absorption spectrum of solutions of manganese dioxide in potassium hydroxide formed after prolonged heating (blue).*



It was not found possible to estimate precise values of $\varepsilon_{max.}$ for Mn^{III} in concentrated alkaline solution because of the tendency of such solutions to disproportionate. However, a series of experiments in which a known quantity of bivalent manganese in aqueous potassium hydroxide was carefully oxidised with oxygen gave a value of about 340. This is undoubtedly a lower limit, but is probably correct to within 20%. The result is comparable with values of $\varepsilon_{max.}$ derived from other tervalent manganese complexes in other media.

Experiments starting from potassium permanganate by procedure (*b*) gave less Mn^V and more Mn^{III} than required for an equimolar mixture, probably owing to partial reduction beyond the Mn^{IV} stage by hydrogen peroxide.

Magnetic Studies.—No electron spin resonance absorption, even at 20° K, was obtained from either green or blue solid solutions prepared from pyrolusite. It has been established that hypomanganate does not absorb detectably under these conditions,[1] and for similar reasons detectable resonance absorption would not be expected for Mn^{III} complexes. The six isotropic hyperfine lines characteristic of the ^{55}Mn nucleus are readily detected at room temperature from melts containing bivalent manganese. This confirms the absence of any Mn^{II} in the blue or green solutions.

Measurements of electron spin resonance spectra were made at 1·25 cm. wavelength as previously described.[1]

[10] Ibers and Davidson, *J. Amer. Chem. Soc.*, 1950, **72**, 4744.
[11] Drummond and Waters, *J.*, 1953, 435.

DISCUSSION

Eliot and Storer's interpretation [7] that dissolution of manganese dioxide in alkali under nitrogen, at 180°, gave manganate, is in error. The green solution first formed has a variable spectrum typified in Fig. 1. We suggest that the sharp rise in the 400—500 mμ region is caused by colloidal, hydrated manganese dioxide, and that some disproportionation has already occurred. The band from Mn^{III} is presumably hidden by the absorption of the colloid. The band at 650 mμ is ascribed to MnO_4^{3-}, the apparent shift from 670 mμ being caused by the superposition of the colloid band.

There is, however, an alternative explanation. Cartledge and Ericks [12] isolated a dark green oxalato-complex of quadrivalent manganese, and recorded its spectrum in aqueous solution; this is qualitatively similar to that given in Fig. 1. The complex ion is formulated as $[Mn^{IV}(C_2O_4)_2(OH)_2]^{2-},2H_2O$ and the manganese is undoubtedly hexaco-ordinated. It therefore seemed possible that the green colour was due to a hexaco-ordinated quadrivalent manganese ion, possibly $Mn(OH)_6^{2-}$.

The electron spin resonance results are not in accord with this formulation. The ion $Mn(OH)_6^{2-}$ is isoelectronic with $Cr(OH)_6^{3-}$, both ions having three $3d$ electrons which half fill the d_ϵ level. One would expect, therefore, a temperature-independent isotropic absorption, similar to that obtained from bivalent manganese. Experimental justification for this expectation comes from the observation that tervalent chromium in a similar "glass" absorbs strongly at room temperature.[8] We therefore conclude that hexaco-ordinated quadrivalent manganese is not responsible for the green colour. It is conceivable that a tetrahedral form of quadrivalent manganese is present, but in view of the uncertainty concerning the electronic structure of tetrahedral ions of this type, mentioned above, no conclusions can be drawn from electron spin resonance results on this point.

However, the ultimate exclusive formation of hypomanganate and tervalent manganese shows that Mn^{IV} is thermodynamically unstable in this medium, and it would be very surprising if the disproportionation (3) occurred slowly at high temperatures. We therefore favour our original interpretation.

Disproportionation.—The disproportionations

$$2MnO_4^{3-} \longrightarrow MnO_4^{2-} + Mn^{IV} \qquad (1)$$

and

$$2Mn^{III} \longrightarrow Mn^{IV} + Mn^{II} \qquad (2)$$

are well established and proceed to completion under ordinary conditions. Our results show, that, under conditions such that polymerisation and precipitation of quadrivalent manganese is prevented, the converse is true and the reaction

$$2Mn^{IV} \longrightarrow MnO_4^{3-} + Mn^{III} \qquad (3)$$

is virtually complete. Thus the reactions (1) and (2) are governed by the stability of polymeric manganese dioxide and by the fact that this is a solid phase. Evidently monomeric Mn^{IV} with oxide or hydroxide ligands is a very reactive species. This conclusion is in accord with an earlier discussion concerning the mechanism of reactions which result in the formation of manganese dioxide,[9] and we stress that such reactions are unlikely to proceed *via* the formation of monomeric quadrivalent manganese.

Results of kinetic studies by Merz, Stafford, and Waters,[13] involving the reduction of permanganate to Mn^{II}, suggest that Mn^{IV} species are those effective in the oxidation of

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[12] Cartledge and Ericks, *J. Amer. Chem. Soc.*, 1936, **58**, 2069.

[13] Merz, Stafford, and Waters, *J.*, 1951, 638.

alcohols. Our results support the mechanism postulated by Waters *et al.* rather than the alternative by Adler and Noyes.[14] Also such steps as

$$2\text{Mn}^{\text{VI}} + \text{Mn}^{\text{II}} \text{———} 2\text{Mn}^{\text{IV}} \text{ (monomeric)}$$ [14]

are improbable unless certain complexing reagents are present which greatly stabilise quadrivalent manganese.

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[14] Adler and Noyes, *J. Amer. Chem. Soc.*, 1955, **77**, 2036.