

921. *Structure and Reactivity of the Oxy-anions of Transition Metals. Part II.* Investigations by Electron-spin Resonance.*

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Electron-spin resonance absorption spectra are reported for certain tetrahedral oxy-anions of manganese, iron, chromium, ruthenium, and rhenium containing either one or two unpaired electrons. The results are discussed in terms of an orbital level scheme recently proposed by Wolfsberg and Helmholz¹ for the ions MnO_4^- , CrO_4^{2-} , and ClO_4^- .

ONE of the most direct applications of electron-spin resonance is to compounds of the transition-group elements where the unpaired electrons are located largely in the inner shells of the particular atoms concerned. A study of their characteristics will thus give considerable information about the valency and energy state of the paramagnetic atom together with details of the bonding to its nearest neighbours. Examples of this type of work are the measurements on different ferric compounds to show the transition from ionic to covalent bonding,^{2,3} and the results obtained from the chloroiridate ion⁴ and

* Part I, *J.*, 1956, 3373.

¹ Wolfsberg and Helmholz, *J. Chem. Phys.*, 1952, **20**, 837.

² Bagguley, Bleaney, Griffiths, Penrose, and Plumpton, *Proc. Phys. Soc.*, 1948, **61**, 542.

³ Bleaney and Ingram, *ibid.*, 1952, **65**, 953.

⁴ Griffiths and Owen, *Proc. Roy. Soc.*, 1954, *A*, **226**, 96.

similar compounds, where the amount of electron-transfer and π -bond character can be accurately calculated.

A study of the oxy-anions of the transition-group elements might therefore throw additional light on their oxidation states and chemical bonding. These systems are not always the best to study by electron-resonance techniques since the compounds are usually stable only in concentrated alkaline solution and often can only be obtained easily in an alkali glass or in an amorphous form. Hence all the additional information available from angular variation in a single crystal is not readily obtained. Nevertheless, the variation of resonant absorption with temperature, and the effective spin value of the ground state can be used to give some information on the likely oxidation state and electronic structure of the paramagnetic atom and be correlated with chemical data.

This differentiation between oxidation states arises from the fact that different energy-level schemes are associated with ions containing different numbers of unpaired electrons. Thus, if it can be shown that the electron-resonance absorption results will only fit into a certain energy-level pattern and that this corresponds to a certain configuration, then the oxidation state of the atom is immediately confirmed. The factors of interest are therefore those from which the complex energy-level pattern of the ion can be deduced. Variation of the resonance line width with temperature is one such important factor. This arises from the fact that the Debye waves of the lattice can only share energy with the spin system *via* a coupling to the orbital motion of the electrons. If such coupling is strong, the compound will have to be cooled to very low temperatures before narrow absorption lines are obtained, and this implies that there are orbital levels quite close to the ground state for such strong spin-orbit interaction to be possible. Conversely, if it is found that the line width is independent of temperature, then the spin-orbit coupling must be very small and there must be a large splitting between the ground state and the next orbital level. It can be seen that a measurement of the variation of line width with temperature can therefore be used to distinguish between different energy-level patterns.

Another factor which will help to determine the energy-level pattern of the ion is the effective spin value of the ground state. This determines the number of electronic transitions which will be observed and can thus be very easily determined from measurements on a single crystal. Since one or more of the transitions may vary with orientation, more care has to be observed in interpreting the results obtained from a glass or powder, as those transitions will have been spread over a large field variation and may thus not be observed. Additional information can also be obtained from the *g*-values of the electronic transitions which measure the rate of divergence of the electronic levels with magnetic field. Similarly, the hyperfine interaction with the nuclear moments of the atom can also be used since both of these depend on the orbital-level splitting to some extent.

It is therefore possible by correlating all the observed facts to draw up a tentative energy-level pattern for the ion, and this is usually precise enough to distinguish one configuration from any possible alternative.

Results.—Table 1 lists the oxy-anions studied together with the paramagnetic results obtained. The ions are classified according to the number of unpaired electrons. Before considering the individual results in detail, we describe the energy level patterns for each configuration, together with the particular effects that each has on the observed electron-resonance absorption associated with the ground state.

For a tetrahedral XO_4 complex, Wolfsberg and Helmholz⁴ have calculated the energies of molecular orbitals formed from linear combinations of *d*, *s*, and *p* atomic orbitals on the X atom and *p* orbitals on the oxygen ligands. Their results for MnO_4^- and CrO_4^{2-} are qualitatively very similar and suggest that the same level scheme would be applicable to other oxy-anions of the transition metals, particularly since McGlynn and Kasha⁵ have recently come to similar conclusions concerning the interpretation of the visible and ultra-violet absorption spectra of many oxy-ions including MnO_4^- and CrO_4^{2-} . On the scheme proposed by Wolfsberg and Helmholz the 24 "valence electrons" of a complex like MnO_4^- completely fill a number of levels to produce a "closed-shell" structure. The next

⁵ McGlynn and Kasha, *J. Chem. Phys.*, 1956, **24**, 481.

lowest-lying unfilled level, which these authors refer to as ($3t_2$), consists of three degenerate molecular orbitals transforming under the representation T_2 of the tetrahedral group T_d . These are formed from d_{xy} , d_{yz} , d_{xz} orbitals on the central atom in antibonding combinations with π -type orbitals on the ligands, and Wolfsberg and Helmholz are able to interpret the visible and ultraviolet absorption spectra of MnO_4^{2-} and CrO_4^{2-} in terms of excitation of electrons into this $3t_2$ level.

TABLE 1. *g-Values of the transition-metal oxy-anions.*

| No. of unpaired electrons | 1 | | 2 | | |
|---------------------------|-------------|-----------------|---------------------------|-------------------|------|
| | g_{\perp} | g_{\parallel} | g | cm.^{-1} | |
| MnO_4^{2-} | 1.97 | 1.95 | MnO_4^{2-} | 2.0 | 0.01 |
| CrO_4^{2-} | 1.97 | 1.98 | RuO_4^{2-} | 2.0 | 0.02 |
| ReO_4^{2-} | 1.95 | 2.00 | ReO_4^{3-} | 2.08 | 0.12 |
| | | | FeO_4^{3-} | $g = 2.14-2.00$ | |

One may conclude from these results that further electrons fed into a complex of this type will be accommodated in the $3t_2$ level which is altogether capable of holding six electrons. Thus transition-metal complexes similar to MnO_4^{2-} would have the electronic configuration (closed-shells) ($3t_2$)¹, whilst those similar to MnO_4^{3-} would have two electrons in the $3t_2$ level.

If it is assumed that the state of least energy obtained from the configuration ($3t_2$)ⁿ is the one which has the maximum spin compatible with the Pauli principle,⁶ then the ground states arising from the configurations mentioned above are as follows:

(a) ($3t_2$)¹. The ground state consists of three orbital states (transforming under the representation T_2 of T_d), each of which has a double spin degeneracy. The orbital degeneracy will be lifted by perturbations arising from distortions of the tetrahedron and from external crystalline fields, but the splitting will be comparatively small. Thus it would be expected that the lowest state of a complex of this type will be doubly degenerate (spin degeneracy) and will lie fairly close to the first excited states.

Application of an external magnetic field will remove the spin degeneracy, and a single electronic transition between the two states of the ground doublet is possible. Because of the other low-lying levels the line width of the absorption should vary markedly with temperature.

(b) ($3t_2$)². The ground state consists of three orbital states (transforming under the representation T_1 of T_d), each of which has a triple spin degeneracy arising from the presence of two unpaired electrons ($S = 1$). Perturbations due to distortions of the tetrahedron, etc., will remove the orbital degeneracy, and the spin degeneracy may also be partly lifted even in the absence of an external field. An external field will remove any remaining degeneracy in the ground state, and two electronic transitions will be possible. If there is a zero field splitting, these two transitions may be shifted relative to each other so that they do not overlap and two separate absorption lines will be obtained. Because of the other low-lying levels the width of these lines will be dependent on temperature.

An argument based on crystal-field theory leads to rather different conclusions. In this approach, the unpaired electrons are considered as being located entirely in d orbitals on the central metal atom, the ion being pictured as built up from a central positive ion and four oxide ligands (O^{2-}). The effect of the electric field produced by these four ligands in a tetrahedral arrangement round the central metal atom is to split the five d levels of the central atom into a group of two ($d\gamma$) levels lying below the remaining three ($d\epsilon$) levels. If this splitting is applied as a perturbation to the lowest term arising from the ground configuration of the free ion, the results shown in Table 2 for differing numbers of unpaired d electrons are obtained. The table also shows results for an ion with six ligands arranged in an octahedron.⁷ From the table it is evident that one can only expect narrow absorption lines at all temperatures from d^2 and d^5 tetrahedral complexes and d^3 and d^5 octahedral complexes.

⁶ Stevens, *Proc. Roy. Soc.*, 1953, A, 219, 542.

⁷ van Santen and van Wieringen, *Rec. Trav. chim.*, 1952, 71, 420.

The detailed results obtained from the different oxy-anions can now be considered and compared with the above conclusions.

(a) MnO_4^{2-} , ReO_4^{2-} , and CrO_4^{3-} . The paramagnetic resonance absorption spectra from all three of these complexes were found to consist of a single line which could only be observed at $T = 20^\circ \text{K}$. The rapid increase of line width with temperature, together with the effective spin value of $\frac{1}{2}$, is in agreement with the deductions made above and confirms that each of the compounds studied did in fact contain one unpaired electron.

TABLE 2.

| Configuration | Spin degeneracy | Orbital degeneracy : | |
|---------------|-----------------|----------------------|------------|
| | | tetrahedron | octahedron |
| d^1 | doublet | doublet | triplet |
| d^2 | triplet | singlet | triplet |
| d^3 | quartet | triplet | singlet |
| d^4 | quintet | triplet | doublet |
| d^5 | sextet | singlet | singlet |

The line shape was asymmetrical in each case, with a prominent shoulder on the side of the peak. This may be interpreted as a g -value variation, and the extreme values are listed in Table 1, the \perp suffix being associated with the peak, and the \parallel suffix with the shoulder. In the case of the manganate ion it has been found possible to make measurements on diluted single crystals and very much more information is thus available. The hyperfine structure from the $I = 5/2$ of the ^{55}Mn isotope can be clearly resolved and is found to be very anisotropic with extreme splittings of $150 \times 10^{-4} \text{ cm.}^{-1}$ and $25 \times 10^{-4} \text{ cm.}^{-1}$. A detailed analysis of these results will be published later.

(b) MnO_4^{3-} , ReO_4^{3-} , and RuO_4^{2-} . The most distinctive and readily interpretable electron-resonance spectrum in this group is obtained from the ruthenate ion. Two distinct electronic transitions are obtained, each with a slight spread but centred on apparent g values of 2.05 and 2.00 at 1.25 cm. wavelength. The separation is probably due to zero-field splitting of the spin triplet, and the two transitions have probably the same g value and a nearly isotropic splitting of 0.02 cm.^{-1} . This is in agreement with the postulated $(3t_2)^2$ configuration of the ruthenate ion. The absorption obtained from the hyporhenate ion is spread continuously over a relatively large field, its extremes corresponding to apparent g values of 2.50 and 2.08. This continuous range of absorption is probably to be attributed to the angular variation in splitting, however, and should thus be interpreted as arising from two electronic transitions with zero-field splitting varying from 0.00 cm.^{-1} up to 0.12 cm.^{-1} . Only one broad line of 600 gauss width is obtained from sodium hypomanganate ($\text{Na}_3\text{MnO}_4 \cdot 10\text{H}_2\text{O}$), but on dilution of the sample this absorption completely disappears. It would seem that this must be attributed to the sensitivity of the spin-triplet splitting to any irregular field symmetries which may arise in the diluted sample. These might well produce zero-field splitting so large that electron resonance is not possible with the frequencies available. Even this negative result is of use, however, since it is only configurations with an even number of unpaired electrons that can have all their degeneracy so removed by the action of internal electric fields. Each of the absorption lines obtained from the three ions was found to be temperature dependent. The MnO_4^{3-} ion had to be cooled to $T = 90^\circ \text{K}$ before the signal was seen, whilst the lines obtained from RuO_4^{2-} and ReO_4^{3-} were only seen at $T = 20^\circ \text{K}$. This temperature dependence is what one would expect from a $(3t_2)^2$ configuration, but it is incompatible with the d^2 configuration of crystal field theory which would exhibit a line width independent of temperature.

The absorption signals obtained from the ferrate ion were of particular interest as there appeared to be a marked change of g value with temperature, from 2.14 at 20°K to 2.00 at 193°K . There also appears to be an appreciable difference between the absorption obtained from BaFeO_4 and K_2FeO_4 . These results do not fit into the pattern outlined for covalent oxy-anions with two unpaired electrons and this problem is being studied in more detail.

EXPERIMENTAL

Electronic Technique.—It has been seen that one of the main features of interest in this work is the variation of the electron-resonance spectra with temperature. Low-temperature resonators have therefore been employed working at 1.25 cm. or 8 mm. wavelengths. These were of the standard type⁸ employing nickel-silver wave-guide feed to a cylindrical cavity operating in the H_{111} mode, and were immersed in a tailed Dewar flask containing liquid oxygen, nitrogen, or hydrogen. The oxy-ion sample was placed centrally in the bottom of the cavity in the region of maximum microwave magnetic field, and normal crystal-video⁹ methods of detection and display were employed. In this way the absorption lines can be observed directly on an oscilloscope screen, and the shape and width measured and photographed.

Preparation of Samples.—All reagents used were of "AnalaR" grade.

Solid potassium manganate was prepared and purified as described in Part I.¹⁰ Potassium manganate-potassium sulphate mixed crystals were obtained from aqueous solutions of potassium hydroxide (4M), saturated with potassium sulphate at room temperature and containing potassium manganate at a concentration of about 10^{-2} M. This solution was concentrated rapidly by evaporation in an evacuated desiccator over potassium hydroxide pellets, and one of the very small crystals obtained on filtration was then used to seed the mother-liquor. This was concentrated slowly by bubbling through it a slow stream of purified dry nitrogen. By this simple method water vapour was slowly removed from the solution, carbon dioxide was excluded, and very gentle agitation of the solution was provided. Single crystals up to 4 mm. long were obtained.

Crystalline hydrated sodium hypomanganate was prepared as described in Part I.¹⁰ Specimens of hypomanganate in an alkali glass were made by dissolving potassium permanganate in molten potassium hydroxide with access to air and cooling the hot blue solutions as rapidly as possible.

Dilute solutions of quinquevalent chromium were prepared in hot concentrated potassium hydroxide solution from potassium chromate. These solutions solidified to glasses at room temperature. No attempt has been made to isolate a crystalline derivative because of the extreme instability of the ion concerned. It is considered most probable that these green solutions contain the hypochromate CrO_4^{3-} ion. Details of the methods used for the preparation and the chemical procedures used to establish the valence state of this ion will be published separately.¹¹

Solid potassium ferrate was prepared and purified by the method described by Hrostowski and Scott¹² and analysed as described by Schreyer.¹³ The resulting solid was found to be at least 95% pure. Mixed microcrystals of potassium ferrate-potassium sulphate were obtained by saturation of an aqueous alkaline potassium ferrate solution with potassium sulphate and precipitation with solid potassium hydroxide. Barium ferrate was precipitated from a dilute alkaline solution of potassium ferrate by addition of barium chloride.

Sodium ruthenate was prepared in an alkali glass by dissolving finely divided ruthenium metal in molten sodium hydroxide and adding sodium peroxide.¹⁴ The resulting solid dissolved in aqueous sodium hydroxide to give a clear orange solution which had an absorption spectrum identical with that described by Connick and Hurley¹⁵ for the ruthenate ion.

Barium rhenate was obtained by fusion of barium per-rhenate (0.22 g.), rhenium dioxide (0.07 g.), and sodium hydroxide (1 g.) *in vacuo*.¹⁶ The green mass was extracted with ethanol, leaving the insoluble barium rhenate as a dark green powder. By using a slight excess of per-rhenate it was ensured that no lower paramagnetic oxidation states of rhenium were present.

Potassium hyporhenate was prepared in an alkali glass by fusion of rhenium dioxide with the theoretical weight of potassium per-rhenate in molten potassium hydroxide *in vacuo*. No attempt was made to isolate the crystalline salt, since it is extremely unstable if free from alkali.

In order to ensure that the electron-resonance absorption lines studied were due to the

⁸ Ingram, "Spectroscopy at Radio and Microwave Frequencies," Butterworths Scientific Publications, London, 1955, p. 66.

⁹ *Op. cit.*, p. 94.

¹⁰ Carrington and Symons, *J.*, 1956, 3373.

¹¹ Bailey and Symons, unpublished work.

¹² Hrostowski and Scott, *J. Chem. Phys.*, 1950, **18**, 106.

¹³ Schreyer, *Analyt. Chem.*, 1950, **22**, 691, 1426.

¹⁴ Krauss, *Z. anorg. Chem.*, 1924, **132**, 309.

¹⁵ Connick and Hurley, *J. Amer. Chem. Soc.*, 1952, **74**, 5012.

¹⁶ I. Noddack and W. Noddack, "Das Rhenium," Voss, Leipzig, 1933, p. 58.

oxy-anions as recorded, several checks were made. Thus in measuring the magnetic susceptibility of potassium ferrate, Hrostowski and Scott¹² found a marked field strength dependence and concluded that this was due to a ferromagnetic impurity, possibly ferric oxide or a ferrite. As a check on the behaviour of these possible impurities an aqueous solution of potassium ferrate was allowed to decompose to ferric oxide. In a second experiment potassium ferrate was allowed to decompose in very concentrated alkaline solution to give a solid solution of ferrite at room temperature. Neither of these samples showed any electron resonance either at room or at liquid-oxygen temperature.

In order to distinguish the signal obtained from the Cr^V ion from that caused by any Cr^{III} impurity, chromic chloride was dissolved in hot concentrated alkaline solution under oxygen-free conditions and cooled to a pale green glass. This gave a signal at room temperature, whereas the signal obtained from Cr^V was not seen above liquid-hydrogen temperatures.

In connection with the results obtained for the rhenate and hyporhenate ions, no resonance could be observed from rhenium dioxide.

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