859. *Structure and Reactivity of the Oxyanions of Transition Metals. Part XVI.* Paramagnetic Ions of Vanadium, Chromium, and Manganese in Sulphuric Acid and Oleum.*

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Compounds, containing a range of valency states, of vanadium, chromium, and manganese dissolved in sulphuric acid and oleums have been studied by magnetic, spectrophotometric, and conductometric methods. In particular, sulphate complexes of quinquevalent chromium and quadrivalent manganese have been identified. The structures of these and related complexes are discussed.

The nature of the complexes formed when "closed-shell" oxyanions of vanadium, chromium, and manganese are dissolved in 100% sulphuric acid and oleums of various strengths has been discussed in Part XIV.[1] Several of these complexes decompose with evolution of oxygen to give lower valency states of the metals,[2] and in the present paper analytical data relating to the final products are presented and structural implications of magnetic, spectrophotometric, and conductometric results are considered.

For purposes of identification and comparison we have also studied quadrivalent and tervalent vanadium, tervalent chromium, and quadrivalent, tervalent, and bivalent manganese salts in these media.

Several quadrivalent vanadyl compounds have been studied by electron spin resonance spectroscopy, including potassium vanadyl oxalate,[3] vanadylætioporphyrin II,[4] and V^{4+} in titanium dioxide.[5] In the first two complexes vanadium is strongly bonded to one oxygen atom, and the similarity in magnetic properties of these compounds to those of acidic aqueous solutions of quadrivalent vanadium provides good evidence in support of the theory that the species in solution is the hydrated vanadyl cation, VO^{2+}. Ballhausen and Gray [6] recently marshalled support from electronic spectral studies for this concept, and showed thereby that the vanadyl ion is probably weakly co-ordinated to four molecules of water in the xy-plane (the V–O bond being taken as the z-direction) and possibly still more weakly to another water molecule which completes an irregular octahedron of ligands about the vanadium atom.

Our results for quinquevalent chromium are discussed in terms of Ballhausen and Gray's proposed energy-level scheme for vanadyl ion, and we add some evidence from infrared measurements in support of their model.

Very recently, Kon [7] reported the detection of spin-resonance absorption from solutions of chromium trioxide in sulphuric acid and he tentatively assigned this to unspecified quinquevalent chromium species. He also gave the g-value and ^{53}Cr isotropic hyperfine coupling constant for solutions of a complex thought to be $CrOCl_4(pyridine)^-$ (Table 2). Hare *et al.*[8] reported a g-value of 1·986 for the compound Rb_2CrOCl_5, but, since this result was not in accord with their expectation, they assigned the spectrum to tervalent chromium impurities.

Experimental and Results

Materials.—"AnalaR" reagents were used without further purification. Oleums were prepared as described previously.[9]

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* Part XV, *J.*, 1963, 4331.

[1] Mishra and Symons, *J.*, 1962, 4411.
[2] Mishra and Symons, *Proc. Chem. Soc.*, 1962, 23.
[3] Golding, *Mol. Phys.*, 1962, **5**, 369.
[4] Roberts, Koski, and Caughey, *J. Chem. Phys.*, 1961, **34**, 591.
[5] Gerritsen and Lewis, *Phys. Rev.*, 1960, **119**, 1010.
[6] Ballhausen and Gray, *Inorg. Chem.*, 1962, **1**, 111.
[7] Kon, *J. Chem. Phys.*, 1962, **35**, 2054.
[8] Hare, Bernal, and Gray, *Inorg. Chem.*, 1962, **1**, 831.
[9] Arotsky, Mishra, and Symons, *J.*, 1961, 12.

Measurements.—Ultraviolet spectrophotometric, magnetic, and conductance measurements were made as described previously.[9] Electron spin resonance spectra were measured with a 3 cm. wavelength spectrometer.[10] Infrared spectra were measured with a Unicam S.P. 100 spectrophotometer, the precautions outlined previously [11] being observed.

Magnetic Susceptibilities.—Typical results, obtained at room temperature, and expressed in terms of the molar susceptibility X_m and the effective magnetic moment $\mu_{\text{eff.}}$, are given in Table 1.

TABLE 1.

Magnetic susceptibilities.

Valency state	Possible formula *	Solvent	$10^6\chi_M$ (20°)	$\mu_{\text{eff.}}$ (B.M.)
$+5$ ($3d^1$)	$OCr(HS_2O_7)_3$	None	1205—1390	1·67—1·80
,,	,,	65% Oleum	1470 ± 150	1·85 ± 0·1
$+4$ ($3d^1$)	$V(HS_4O_4)_4$	100% H_2SO_4	1105 ± 125	1·6 ± 0·1
$+3$ ($3d^3$)	$Cr(HS_2O_7)_3$	65% Oleum	5470 ± 300	3·6 ± 0·1
$+4$ ($3d^3$)	$Mn(HS_2O_7)_4$	65% Oleum	5510 ± 360	3·64 ± 0·15

* Co-ordinated solvent molecules are not included.

TABLE 2.

Electron spin resonance data.

Compound	$g_{/\!/}$	$g_{\perp}$	g_{av}	$\|A_{\text{iso}}\|$ (gauss)	Temp.	Ref.
Cr^V 65% Oleum)	1·951	1·970	1·964		R.T.	*a*
,, ...	1·936	1·986	1·964		77°K	*a*
Cr^V (30% Oleum) (i)	—	—	1·970	23 (^{53}Cr)	75°K	*a*
(ii)	—	—	1·965	23 ,,	,,	*a*
Cr^V (100% H_2SO_4) (i)	—	—	1·970	23 ,,	,,	*a*
(ii)	—	—	1·965	23 ,,	,,	*a*
$CrOCl_4$ (Pyridine)$^-$	—	—	1·9875	20	R.T.	7
Rb_2CrOCl_5(?)	—	—	1·986	—	R.T.	8
Cr^{III} (100% H_2SO_4; oleum) ...	No detectable absorption from green solutions					
Mn^{IV} (65% Oleum)	—	—	2·00	100	R.T.	*a*
Mn^{II} (100% H_2SO_4)	—	—	2·00	96	R.T.	*a*
V^{IV} (Aq.H_2SO_4)	—	—	1·962	116	R.T.	*a*
V^{IV} (100% H_2SO_4; oleum) ...			No detectable absorption			
$VO(C_2O_4)^{2-}$	1·940	1·972	1·961	103 *	R.T.	3

* $|A_{/\!/}| = 180$, $|A_{\perp}| = 65$ gauss. (A_{iso} is given as 117 gauss in ref. 3 but this appears to be the result of an error in calculation.)

a, This work. R.T. = room temperature.

Electron Spin Resonance Spectra.—Results are summarised in Table 2 together with typical results for other $3d^1$ complexes. Selected spectra are reproduced in Figs. 1 and 2.

Spectra attributed to quinquevalent chromium complexes in 100% sulphuric acid and dilute oleums were broad and asymmetric at room temperature but well resolved at 70—75°, the width between points of maximum slope being then in the region of one gauss. Under these conditions two intense lines of variable relative intensities and separated by between 5 and 10 gauss were detected for acids in the range 100% sulphuric acid to 30% oleum, but only one intense line was observed for solutions in 65% oleum. These lines are attributed to two $^{52}Cr^V$ complexes having different ligands but very similar symmetry and bonding In addition, weak lines attributed to complexes containing ^{53}Cr were detected. In general, six of the expected eight lines appeared, having a progressive broadening on going from low to high field (Fig. 1). This broadening was so marked that early spectra showed only the pair at lowest field and, since the intensities of these, relative to the central components, were far larger than expected for ^{53}Cr, we originally attributed them to two further $^{52}Cr^V$ complexes in low concentration having slightly modified environments. This mistake also appears to have been made by Kon.[7] Recognition that the separation between these low-field lines was identical with that between the intense pair and that relative intensities within each doublet were almost identical led us to examine the spectra at elevated temperatures and under high gain. Further lines were then detected (Fig. 1). The remaining two of the expected eight

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[10] Brivati, Keen, and Symons, *J.*, 1962, 237.

[11] Arotsky, Mishra, and Symons, *J.*, 1962, 2582.

satellite lines are hidden under the intense central components. When the average intensity of either quartet was compared with that of the corresponding central line, results close to that expected for ^{53}Cr were obtained.

Spectra from quinquevalent chromium in rigid solutions of 65% oleum at 77°K (Fig. 2) were characteristic of complexes having an axis of symmetry, and magnitudes of the g-tensor were obtained therefrom in the normal way. Features from complexes containing ^{53}Cr were so poorly recorded that attempts to derive principal values for the hyperfine tensor failed.

Violet salts of hydrated tervalent chromium gave broad spectra in 100% sulphuric acid, identical with spectra obtained from aqueous solutions. Intensities slowly decreased, however, and the spectra were lost after about two hours, by which time the solutions were green. Similar green solutions resulted directly on dissolution of these salt in 65% oleum, and no spin-resonance spectra could be detected.

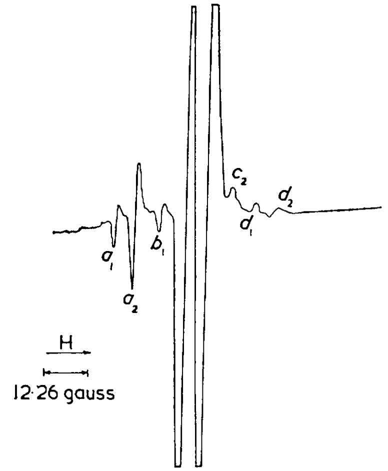

FIG. 1. First derivative of the electron spin resonance spectrum of quinquevalent chromium in 30% oleum at 75° and high gain. The sets a_1—d_1 and a_2—d_2 are hyperfine components arising from complexes containing ^{53}Cr. Lines 1 and 2, associated with complexes containing the more abundant ^{52}Cr isotope, have an intensity ratio identical with that for a_1 and a_2. Hyperfine components c_1 and b_2 are hidden under these intense lines.

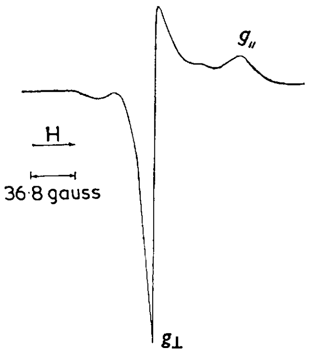

FIG. 2. First derivative of the electron spin resonance spectrum of quinquevalent chromium in 65% oleum at 77°K.

Sextets of overlapping equally spaced lines were detected from solutions of quadrivalent manganese in 65% oleum. On cooling to 77°K, these were better resolved but no indication of other components of the expected fine structure triplet could be detected. Bivalent manganese salts gave similar spectra at room temperature in 100% sulphuric acid, but their solubility in 65% oleum was so small that no spin-resonance spectra could be observed.

The characteristic asymmetric spectrum of eight hyperfine lines was found for quadrivalent vanadium in aqueous sulphuric acid but no resonance was obtained from solutions in 100% sulphuric acid or oleums, even at 77°K.

Ultraviolet and Visible Spectra.—For most compounds studied in sulphuric acid and oleums, weak ligand-field bands were detected in the visible region and intense charge-transfer bands in the ultraviolet, their onset being generally between 350 and 400 mμ. Details of the ligand-field bands are listed in Table 3.

Infrared Spectra.—Spectra of vanadyl sulphate in 30% aqueous sulphuric acid and of $(VO)SO_4,5H_2O$ discs were characterised by a strong broad absorption band at 995 cm.$^{-1}$ attributed to the V–O stretching frequency, and by bands in the 1100 cm.$^{-1}$ region attributed

TABLE 3.

Features of visible and ultraviolet spectra.

		1st Band		2nd Band	
	Solvent	$E_{max.}$ (cm.$^{-1}$);	ε	$E_{max.}$ (cm.$^{-1}$);	ε
$Cr^{V}(3d^1)$	65% Oleum	13,700;	60	18,100;	40
$CrOCl_5^{2-}$	Solid salt *	12,900		23,500	
$V^{IV}(3d^1)$	Aq. H_2SO_4	13,230;	18·6	16,200 †;	8
,, ...	100% H_2SO_4	12,800 †;	12	14,500;	18
,, ...	65% Oleum	12,500 ‡;	6	14,900;	14
$Mn^{IV}(3d^3)$	65% Oleum	17,670;	112		
$Cr^{III}(3d^3)$	Aq. H_2SO_4	17,000;	14	25,000;	16
	100% H_2SO_4	14,000;	37	20,830;	30
		14,700;	35		
	65% Oleum	14,100;	40	20,380;	42
		14,700;	34		

* Gray and Hare, *Inorg. Chem.*, 1962, **1**, 363. † Shoulder in this region. ‡ Very poorly defined inflection in this region.

to sulphate. Vanadyl chloride in dilute aqueous hydrochloric acid had a single band at 995 cm.$^{-1}$.

Conductance Results.—These are summarised in Fig. 3. Results for solutions of Cr^{V}, Mn^{IV}, and V^{IV} in 65% oleum suggest that these complexes are neutral, and certainly exclude the possibility that oxycations such as CrO_2^+ or VO^{2+} are formed in this medium.

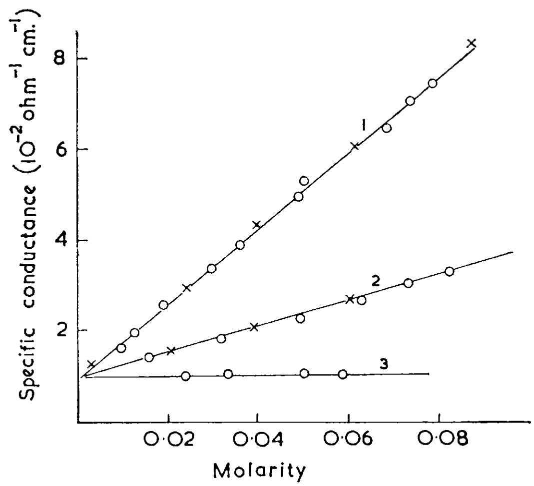

FIG. 3. Specific conductance as a function of molarity for various derivatives of vanadium, chromium, and manganese in 65% oleum.

(1) K_2SO_4 (o), K_2CrO_4 (×), (2) $KHSO_4$ (o), $KMnO_4$ (×), (3) $VOSO_4$ (o).

Evidence for Quinquevalent Chromium.—Identification of the product of reaction between 65% oleum and potassium chromate as a monomeric quinquevalent chromium complex rests upon the following observations: (i) Oxygen evolution was quantitatively in accord with the reaction

$$4Cr^{VI} \longrightarrow 4Cr^{V} + O_2$$

(ii) Spin-resonance absorption was detected from ^{52}Cr and ^{53}Cr at room temperature but not from tervalent chromium under these conditions. It is most unlikely that quadrivalent chromium would give rise to a detectable spin-resonance spectrum under these conditions because any paramagnetic form would be in a triplet spin state and anisotropic spin–spin interactions normally broaden the absorption of such complexes beyond the limits of detection. (iii) The electronic spectrum is in accord with expectation for a $3d^1$ complex. (iv) The magnetic susceptibility is close to that expected for complexes having one unpaired electron per chromium atom on the "spin-only" approximation. This approximation is valid since the principal components of the *g*-tensor were found to be relatively close to the free-spin value.

Identification of the intermediates formed when chromates are dissolved in 100% sulphuric acid as quinquevalent chromium complexes rests entirely on the observation that their spin-resonance spectra are closely similar to those assigned to Cr^V in 65% oleum. It is noteworthy that the green tervalent chromium complex ultimately formed in these solutions gives no detectable spin-resonance absorption.

Evidence for Quadrivalent Manganese.—This is similar to that for quinquevalent chromium: (i) Oxygen evolution, when potassium permanganate reacted with 65% oleum, was in good accord with the equation

$$4Mn^{VII} \longrightarrow 4Mn^{IV} + 3O_2$$

(ii) Manganese dioxide dissolved, without evolution of oxygen, to give blue solutions indistinguishable from those obtained from permanganate. (iii) Spin-resonance absorption was clearly detected at room temperature. None is expected under these conditions from quinque- or ter-valent manganese complexes, or from bivalent manganese since the pyrosulphate is effectively insoluble in the medium. (iv) The magnetic susceptibility corresponds, on the assumption of no orbital contribution, to three unpaired electrons.

DISCUSSION

Quadrivalent Vanadium.—Not all quadrivalent vanadium complexes give narrow spin-resonance spectra at room temperature. Thus no resonance can be detected from the tetrachloride at 77°K, from hydroxy-complexes in aqueous alkali, or sulphate complexes in sulphuric acid. Similarly, whilst the resonance absorption of hexa-aquotitanate(III) broadens beyond the limitations of detection above about 10°K, the difluoro-complex gives rise to narrow lines at room temperature, as does the complex formed by adding methoxide ion to methanolic solutions of Ti^{3+}.[12]

Formally, these results mean that those complexes giving rise to resolved spectra at room temperature have such low symmetry that there is a large energy gap between the ground-state spin doublet and the first excited state, and hence that spin-lattice relaxation is relatively unimportant. Thus if narrow lines are detected at room temperature for d^1 ions this can be taken as diagnostic of such low symmetry. This conclusion requires justification since for symmetrical tetrahedral ions the unpaired electron is in a degenerate orbital doublet[13,14] for which there should be no orbital contribution to the magnetic moment. Since the first excited state is some 15,000 cm.$^{-1}$ above the ground e-level it is not obvious why such complexes should exhibit such efficient relaxation that very low temperatures are required for measurement.[13] This problem has not been studied theoretically, but the experimental evidence is thought to be sufficiently strong to justify the generalisation drawn above. Possibly the relaxation mechanism is associated with the fact that relatively small vibrational distortions of tetrahedral d_1 ions will remove the ground-state orbital degeneracy and thereby induce considerable asymmetry in the hyperfine and g-tensors. A permanent distortion of this sort was found for d^1-tetroxides at 20°K.[13]

We conclude that the fact that relatively narrow lines are obtained in the spin-resonance spectrum of quadrivalent vanadium in acidic solutions is strong evidence in favour of high ligand asymmetry, and supports the model of Ballhausen and Gray. If the z-axis is taken as the V–O direction with the origin at the vanadium atom, there will be a strong σ-bond involving the d_{z^2} level, and strong π-bonds involving d_{xz} and d_{yz}. In this approximation the d_{xy} and $d_{x^2-y^2}$ levels are degenerate, but the presence of four ligands lying along or close to the x- and y-axes will lift this degeneracy, and, if the resulting σ- and π-bonding is relatively weak, the final level scheme is expected to take the form given in Fig. 4. The presence of an extra, weakly bonded ligand in the sixth position is unlikely to alter the sequence of levels. This scheme is similar to that discussed by

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[12] Waters and Maki, *Phys. Rev.*, 1962, **125**, 233.

[13] Carrington, Ingram, Lott, Schonland, and Symons, *Proc. Roy. Soc.*, 1959, *A*, **254**, 101.

[14] Carrington and Symons, *Chem. Revs.*, 1963, **63**, in the press.

Ballhausen and Gray[6] but differs from that of Golding[3] for the bisoxalato-derivative. That d_π–p_π bonding between the metal and oxygen is likely to be important follows from the results derived from various tetroxides[13,14] and, for example, from studies[15] of the osmate ion, $OsO_2(OH)_4^{2-}$. In this ion, π-bonding involving the d_{xz}, d_{yz} level is so strong that the two " outer " electrons are constrained to pair in the d_{xy} orbital.

However, our infrared results[16] do not seem to be in accord with the concept[6] that there are two strong π-bonds to the single oxide ligand. It has been suggested[6,8] that the major reason for the formation of oxycations of this type is the fact that two strong π-bonds can then be incorporated. We dispute the implication[6,8] that such oxycations are of common occurrence, and propose an alternative reason for the formation of the few known ions of this type.

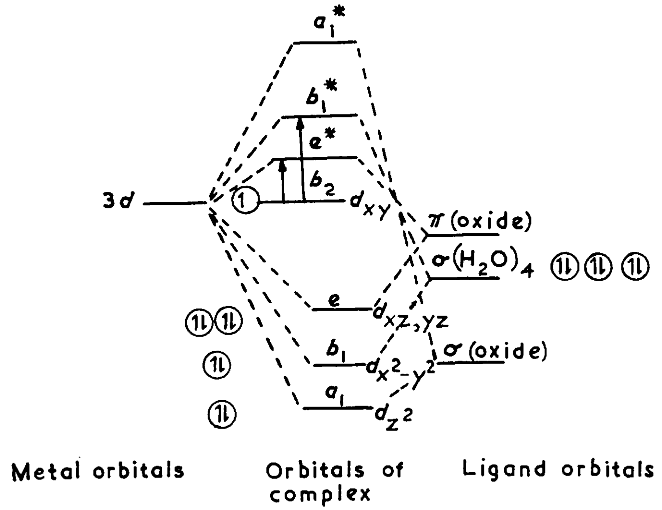

FIG. 4. Relative levels of molecular orbitals for $VO(H_2O)_5^{2+}$ and related complexes. The z-axis is the V–O direction and four water molecules lie on the x- and y-axes whose origin is close to the vanadium atom. The vertical arrows indicate the electronic transitions discussed in the text.

The essential problem is summarised in the tautomeric change

$$OV(H_2O)_5^{2+} \rightleftharpoons V(OH)_2(H_2O)_4^{2+}$$

Generally we would expect this equilibrium to lie to the right for aqueous solutions. In both complexes two strong π-bonds can be formed, but in the latter these would include two *trans*-hydroxide ligands. We suggest that the equilibrium lies to the left in this case because a Jahn–Teller distortion or a process described as " rattling "[17] becomes " fixed " as a result of a tautomeric change. Thus, when the vanadium atom happens to be close to one hydroxide in the symmetrical complex this will become acidic whilst the other will become basic. Rapid response by the solvent then " fixes " the distortion.

It is significant that such a process does not occur for the larger Ti^{3+} ion in aqueous solution, whereas sexivalent manganese is found as the tetrahedral manganate ion.

The marked change in the visible spectrum together with the loss of spin-resonance absorption for quadrivalent vanadium, on going from aqueous to concentrated sulphuric acid and oleums, suggest that the structure is changed in such a way that the gross

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[15] Lott and Symons, *J.*, 1960, 973.

[16] Barraclough, Lewis, and Nyholm, *J.*, 1959, 3552.

[17] Dunitz and Orgel, " Advances in Organic and Radiochemistry," Academic Press Inc., New York, 1960, p. 1.

dissimilarity between different ligands is largely lost. Furthermore, conductance results show that the species in oleum is uncharged. Possible structures are $V(HSO_4)_4$, $V(HSO_4)_4(H_2SO_4)$, and $V(HSO_4)_4(H_2SO_4)_2$ and the corresponding pyrosulphate derivatives.

Quinquevalent Chromium.—The structure of the stable complex formed by reaction between chromate and 65% oleum is considered in terms of the postulate, justified in the Experimental section, that this is a monomeric derivative of quinquevalent chromium. On consideration of the visible and electron spin resonance spectra, we suggest that this complex is a sulphate or pyrosulphate having one strongly bonded oxide ligand.

There is a close similarity between the visible spectrum of aquated vanadyl ion and those of the chromium complexes (Table 3), with respect to both band energies and their relative intensities. Also spectra of the chromium complexes are comparable with that reported for the salt $(NH_4)_2CrOCl_5$,[18] in the solid state. Further, the differences recorded can be qualitatively understood in terms of the molecular-orbital level scheme adopted for aquated vanadyl ions (Fig. 4). Magnetic and spectral data, in addition to chemical expectation, strongly suggest that hydrogen sulphate and, especially, hydrogen pyrosulphate must be very weakly bonded to transition-metal ions, both with respect to σ- and to π-interactions. Thus, compared[18] with the pentachloro-derivative, $OCrCl_5^{2-}$, the derivative in oleum should have its first band ($d_{xy} \longrightarrow d_{xz,yz}$) at slightly higher energies since the antibonding level involving d_{xy} will be raised in energy as a result of π-bonding with chloride whilst the $d_{xz,yz}$ level which is already involved in π-bonding to oxygen will be but slightly modified on going from one complex to the other. In contrast, the second band for the oleum complex should occur at considerably lower energy than that for the chloro-derivative since this band is identified as $d_{xy}(b_2) \longrightarrow d_{x^2-y^2}(b_1^*)$, and the b_1^* level, being an antibonding σ-level, is expected to be raised in energy on going to the pentachloride. These expectations are well fulfilled (Table 3).

The spin-resonance results are also most satisfactorily interpreted in terms of such a complex. Thus the fact that narrow lines are obtained is in accord with expectation for complexes having asymmetric structures such as $OCr(HSO_4)_3(H_2SO_4)_2$. Also the isotropic hyperfine coupling is close to that expected for an unpaired electron in a 3*d* level, and the values for $g_{/\!/}$, $g_{\perp}$, and g_{av} are also satisfactorily accommodated in this way. This can be seen by comparison with results for comparable vanadyl complexes (Table 2) and also by application of the appropriate equations to the system

$$g_{/\!/} = 2[1l - (C_1^*)^2 4\xi/\Delta E(^2B_2 \longrightarrow {}^2B_1)]$$

and

$$g_{\perp} = 2[1l - (C_1^*)^2 \xi/\Delta E(^2B_2 \longrightarrow {}^2E)]$$

where ξ is the appropriate spin–orbital coupling constant, ΔE the energy of the transitions indicated, and C_1^* the coefficient of the metal orbital in the appropriate level. Substituting the spectral data of Table 3 and the reasonable values of 200 cm.$^{-1}$ and 0·9 for ξ and C_1^* gives $g_{\perp} = 1{\cdot}98$ and $g_{/\!/} = 1{\cdot}93$, in good agreement with experiment. The spin–orbital coupling constant has been reduced to about 50% of the free-ion value, as was done for the vanadyl ion.[6] Thus both the spin-resonance and optical data are in good accord with the structural assignment.

The unstable quinquevalent species detected in 100% sulphuric acid are presumably similar in structure. Two species are clearly differentiated in the spin-resonance spectrum, having closely similar average *g*-values and identical isotropic hyperfine coupling constants (Table 2). These are probably both $OCrX_4$ or $OCrX_5$ species, and we suggest that they differ only in that one has a hydroxy-ligand and the other a hydrogen sulphate ligand.

These postulates are closely similar to those put forward to explain the properties of " closed-shell " oxyions such as permanganate or chromate in sulphuric acid.[1]

Spin-resonance spectra of quinquevalent chromium in sulphuric acid and oleum at room temperature are relatively broad, and the latter show a shoulder characteristic of a

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[18] Gray and Hare, *Inorg. Chem.*, 1962, **1**, 363.

g-value variation. Indeed, the values for $g_{/\!/}$ and $g_{\perp}$ estimated from these spectra fit the equation

$$g_{\mathrm{av}} = 1/3(g_{/\!/} + 2g_{\perp})$$

as do the results for rigid solutions. We conclude that the complexes containing quinquevalent chromium are "tumbling" relatively slowly, so that the g-anisotropy is only partially averaged.

It is significant that the very marked variation in line-width found for the quartet associated with ^{53}Cr at 70° parallels exactly the asymmetry found at lower temperatures, thus showing clearly that this variation is to be associated with the hyperfine and g-anisotropy.

The two quinquevalent chromium species detected in 100% sulphuric acid are not rapidly interconverted, since two narrow sets of spectra are detected. Hence, in terms of the above postulate, reactions of the type

$$\geqslant\mathrm{CrOH} + \mathrm{H_2SO_4} \longrightarrow \geqslant\mathrm{CrOSO_3H} + \mathrm{H_2O}$$

are relatively slow in this medium. This is in agreement with conclusions drawn for the reactivity of tervalent chromium complexes in this medium.

Tervalent Chromium. When the ion $Cr(H_2O)_6^{3+}$ is dissolved in 100% sulphuric acid the optical and spin-resonance absorptions change very slowly, whereas similar changes are extremely rapid in 65% oleum. Since tervalent chromium is inert to nucleophilic substitution and the nucleophilic power of the solvent is negligible, it seems that sulphonation proceeds by electrophilic attack on oxygen, and that this is slow in 100% sulphuric acid but very fast in oleum.

Quadrivalent Manganese.—Evidence that the species formed when permanganate reacts with oleum is a monomeric quadrivalent manganese complex has been given in the Experimental section.

It is curious that, in this medium, no spin-resonance absorption is detected from tervalent chromium but that relatively narrow lines are resolved for isoelectronic quadrivalent manganese. It seems likely that, for manganese, only the $\Delta M_s = \pm\frac{1}{2}$ trasition is detected, the other components being broadened beyond detection because of an anisotropic splitting of the quartet spin-states. This is suggested by the observation that the magnetic susceptibility is indicative of three unpaired electrons whilst the approximate value estimated from the spin-resonance spectrum is one unpaired electron. Also, rigid solutions at 77°K still show a narrow sextet of lines with no indication of fine structure. This suggests strongly that all but the $\Delta M_s = \pm\frac{1}{2}$ transition are broadened beyond detection. These narrow lines show that both the g-value and hyperfine coupling are nearly isotropic, in contrast with results for $3d^1$ compounds. This indicates that the ground state is relatively symmetrical for these complexes.

Bivalent Manganese.—Since there are two positive charges per manganese atom for solutions in 100% sulphuric acid it seems probable that the complex is simply $Mn(H_2SO_4)_6^{2+}$. The isotropic hyperfine coupling of 96 gauss is close to that found for $Mn(H_2O)_6^{2+}$ but is slightly smaller than that for quadrivalent manganese in oleum.

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