270. *Magnetism and Molecular Constitution of Some Chromium Compounds.*

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In the present work an attempt is made to define the structure of some chromium compounds from the magnetic standpoint. The susceptibilities of chromium ions in different valency states were calculated from the Van Vleck, Sommerfeld, Bose, and Stoner formula, $\chi_M = N\beta^2[4s(s + 1)]/3kt$, and compared with the experimental values determined on a modified form of Gouy's balance. Chromium dioxide is shown to contain quadrivalent chromium, the constitution of a complex chromium sulphate has been confirmed, and silver chromate and the pyridine salt of the so-called blue perchromic acid (since shown by Schwarz and Giese to be a derivative

of CrO_5 and not $HCrO_5$) have been shown to contain sexavalent chromium. The supposed sexavalency of chromium in triamminochromium tetroxide and its quinquevalency in pyridinium tetrachlorohydroxychromate, $C_5H_5N{\cdot}CrCl_4{\cdot}OH,H_2O$, and the analogous quinolinium salt have been controverted, more satisfactory constitutions being suggested. The three isomerides of dichloroaquotriamminochromic chloride have been examined from the magnetic standpoint.

THE magnetic method has recently afforded useful information on the valency of particularly the paramagnetic ions. Chromium exists in various valency states, but comparatively little use has been made of this method in defining the structure of compounds of this element. The more important recent investigations are the following.

The paramagnetic properties of some bivalent chromium salts were investigated by Lips (*Helv. Physica Acta*, 1934, **7**, 537). The number of Bohr magnetons was found to be 4·82, in agreement with the value resulting from " spin only," *viz.*, $\sqrt{4s(s+1)} = 4{\cdot}90$.

Leiterer (*Z. physikal. Chem.*, 1937, *B*, **36**, 325) determined the magnetic susceptibility of certain co-ordination compounds of chromium, in which its principal valency is three. He found excellent agreement between theoretical and experimental values on the basis that the orbital moment was fully quenched. This conclusion is in substantial accord with the results of previous workers in this field.

Tjabbes (*Z. anorg. Chem.*, 1932, **210**, 385) showed that the supposed septa- or higher valency, postulated in the case of the blue and the red perchromates, was not in harmony with their magnetic behaviour. He found the value of magnetons in the red perchromates to be very nearly the theoretical value for quinquevalent chromium, resulting from the " spin only," *viz.*, $\sqrt{4s(s+1)} = 1{\cdot}73$. In the blue perchromates, he established the sexavalency of chromium, for this variety exhibited a feeble paramagnetism independent of temperature which is theoretically predicted for this element in the sexavalent state.

It is obvious from the foregoing that the magnetic moment for chromium varies with its state of combination or valency, and the present investigation was, therefore, undertaken in order to elucidate the constitution of some of those chromium compounds of indefinite structure recorded in literature.

EXPERIMENTAL.

The susceptibility determinations were carried out in a modified form of Gouy's balance (Bhatnagar and Bal, *J. Indian Chem. Soc.*, 1934, **11**, 606), and χ was calculated according to the equation

$$\chi_{p_2} = \frac{1}{m_{p_2}}\left\{(\chi_{p_1}m_{p_1} - \chi_a m_{ap_1})\frac{w_{p_2}}{w_{p_1}} + \chi_a m_{ap_2}\right\}$$

where χ_{p_1} and χ_{p_2} are respectively the specific susceptibility of the standard substance and of the specimen, w_{p_1} and w_{p_2} are the respective pulls, m_{p_1} and m_{p_2} are the respective masses, and m_{ap_1} and m_{ap_2} are the masses of air displaced respectively by the standard substance and by the specimen.

The various compounds to be investigated were prepared as follows.

(1) *Brown Product described as* CrO_2 *or* Cr_5O_9.—Dunnicliff and Kotwani (*J. Physical Chem.*, 1931, **35**, 3221) obtained a brown product on treating chromium hydroxide with 5% chromic acid solution. Analysis indicated that the formula of the compound approximated to CrO_2 or Cr_5O_9. In the present investigation this product was dried at 200° and then kept in a vacuum for some time. The dried product (Found: Cr, 62·4, 62·0. Calc. for CrO_2: Cr, 61·9%. Calc. for Cr_5O_9: Cr, 64·35%) had $d_{4^\circ}^{25^\circ}$ 2·645.

(2) *Complex Chromium Sulphate produced by the Action of Chromium Sulphate on Chromium Hydroxide.*—By this means, the same authors (*loc. cit.*, p. 3223) obtained a complex chromium compound containing equal amounts of co-ordinated and ionic sulphate; it was therefore assigned the constitution $[\{Cr_2(OH)_2(H_2O)_7\}_2SO_4]^{\cdot\cdot}SO_4{}'',xH_2O$. In the present investigation, the compound was obtained anhydrous by drying in a vacuum at room temperature [Found: Cr, 28·6; SO_4, 26·4. Calc. for $Cr_4(OH)_4(SO_4)_2(H_2O)_{14}$: Cr, 28·9; SO_4, 26·7%]; $d_{4^\circ}^{20^\circ}$ 2·57.

(3) *Triamminochromium Tetroxide*, $CrO_4,3NH_3$.—The compound was prepared by two methods (Hofmann and Hiendlmaier, *Ber.*, 1905, **38**, 3059): (*a*) A 10% aqueous solution of ammonia was saturated at 0° with crystallised ammonium dichromate, 30% hydrogen peroxide

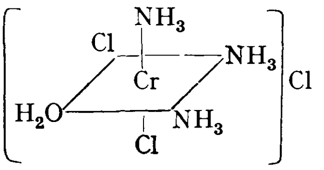
added to the clear solution, and the mixture kept for 6—12 hours; the large brown crystals which separated were freed from a red crystalline powder by allowing the temperature to rise to 10—15° (Found: Cr, 31·2. Calc.: Cr, 31·15%). (*b*) A 20% solution of ammonia was saturated at 0° first with ammonium dichromate and then with ammonia, and 30% hydrogen peroxide added; after some hours the compound was obtained in quadratic plates (Found: Cr, 31·15%). The densities of the two samples at 20° were respectively 1·958 and 1·960, whereas Riesenfeld, Kutsch, and Ohl (*Ber.*, 1905, **38**, 4072) recorded 1·964.

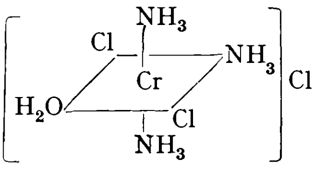
(4) *Silver Chromate.*—Silver chromate, obtained by dropping a dilute solution of potassium chromate into a concentrated solution of silver nitrate (Vauquelin, *Ann. Chim. Phys.*, 1809, **80**, 70), was purified by repeatedly dissolving it in aqueous ammonia and reprecipitating it by boiling the solution. During the process the orange-red chromate changed into the green modification (Found: Ag, 65·3; Cr, 15·45. Calc.: Ag, 65·05; Cr, 15·65%); it had *d* 5·619, whereas Baxter, Mueller, and Hines (*J. Amer. Chem. Soc.*, 1909, **31**, 538) record 5·625. The colour of this variety varies from dark green to greenish-black, but is red in transmitted light or in the powdered form. It has been suggested, but not proved, that the change in colour may be due to a change in crystal structure or the sizes of the crystalline aggregates (Mellor, " Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XI, p. 265).

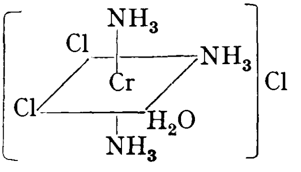
(5) *Pyridinium Tetrachlorohydroxychromate.*—This compound was prepared by the action of concentrated hydrochloric acid and pyridine on chromic acid (Weinland and Fridrich, *Ber.*, 1905, **38**, 3784); it formed reddish-brown leaflets (Found: Cr, 16·7; *M*, cryoscopic in acetic acid, 306. Calc.: Cr, 16·9%; *M*, 308). Since the chromium in this compound behaves as if it were quinquevalent, Weinland and Fridrich assigned to it the constitution $CrCl_4{\cdot}OH{\cdot}C_5H_5N,H_2O$.

(6) *Quinolinium Tetrachlorohydroxychromate*, $C_9H_7N{\cdot}CrCl_4{\cdot}OH,2H_2O$.—This compound was similarly prepared (Found: Cr, 13·8. Calc.: Cr, 13·8%).

(7) *Dichloroaquotriamminochromic Chloride*, $[Cr(NH_3)_3(H_2O)Cl_2]Cl$.—Riesenfeld and Seemann (*Ber.*, 1909, **42**, 4226) report three varieties of this compound, which have since been regarded as isomerides:







They were obtained by the following methods:

(i) *Reddish-violet modification.* This was prepared by adding concentrated hydrochloric acid to a solution of triamminochromium tetroxide in well-cooled dilute hydrochloric acid and allowing the solution to stand for some time. The reddish-violet crystals, *d* 1·498 (Found: Cr, 22·9; total Cl, 46·5. Calc.: Cr, 22·9; Cl, 46·8%), form a blue solution with water.

(ii) *Grey modification.* This variety was obtained by using concentrated instead of dilute acid as above, *d* 1·629 (Found: Cr, 22·8; Cl, 46·7%); it is scarcely soluble in cold water but dissolves in hot water to a red solution.

(iii) *Green modification.* This was obtained in solution by heating a hydrochloric acid solution of the first variety for some time at 60°.

Frowein (*Z. anorg. Chem.*, 1920, **110**, 107) showed from conductivity measurements and from the colour change of the first isomer that the monoaquo-salt gradually passes into the diaquo-salt, and this in turn into the triaquo-salt, the colours of the solutions being blue, reddish-violet, and red respectively. The conductivity of the monoaquo-salt is the lowest, and that of the triaquo-salt the highest. Nevertheless, application of this method to the other isomerides affords no useful information as to their structure, for the aquo-salts derived from them will be identical.

(8) *Pyridine Derivative of Perchromic Acid.*—The compound was obtained by addition of the base to the blue ethereal solution of perchromic acid cooled to 0° (Wiede, *Ber.*, 1897, **30**, 2178) (Found: Cr, 24·7. Calc. for $C_5H_5N,HCrO_5$: Cr, 24·5%). Schwarz and Giese (*Ber.*, 1932, **65**, 871) concluded from its chemical behaviour that the blue compound is not an acid, $HCrO_5$, but is a superoxide of the formula CrO_5. Further confirmation of this view is desirable.

Magnetic Data.—The specific susceptibilities of these compounds were determined in the solid state. In the case of the green modification of compound (7), however, the value was obtained differently. A known weight of the reddish-violet variety was treated with a known volume of hydrochloric acid at 60°, care being taken that there was no loss of acid. The green solution, so obtained, was diluted with water to 1% concentration and its value of χ determined. From this, the mass susceptibility of the solid was calculated by correcting for that of hydrochloric acid. The relationship used was

$$\chi_{\text{soln.}} = c_s\chi_s + (1 - c_s)\chi_{\text{HCl}}$$

where the symbols have their usual significance. In the following table the value of χ in each case represents the mean of at least three observations.

	$\chi \times 10^6$.	Temp.
(1) CrO_2 or Cr_5O_9	35·10	25°
(2) Complex chromium sulphate	34·95	20
(3) Triamminochromium tetroxide obtained by		
(i) first method	21·64	20
(ii) second method	21·60	20
(4) Silver chromate :		
(i) green modification	−0·121	25
(ii) powdered red form	−0·119	25
(5) Pyridinium tetrachlorohydroxychromate	0·32	25
(6) Quinolinium tetrachlorohydroxychromate	−0·13	25
(7) Dichloroaquotriamminochromic chloride :		
(i) reddish-violet modification	28·96	20
(ii) grey modification	28·75	20
(iii) green modification (obtained in HCl soln.)	14·63	20
(8) Pyridine salt of perchromic acid	1·06	30

Further, the susceptibilities of the reddish-violet and the grey modification of (7) were also determined in 1% aqueous solution. The solutions were heated to different temperatures and then cooled to 20°; it was noted that they retained any altered colour that they may have developed on heating. The results are embodied in the following table.

Modification.	Temp. to which soln. was heated.	Colour of soln.	$\chi_s \times 10^6$.*
Reddish-violet	20°	Blue	28·85
	50	Red	28·75
	80	Red	28·75
	98·5	Green	21·73
Grey	50	Red	28·50
	80	Red	28·50
	98·5	Green	22·10

* The susceptibilities of the solids were calculated from the relationship $\chi_{\text{soln.}} = c_s\chi_s + (1 - c_s)\chi_{H_2O}$.

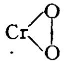
Discussion of Results.

(1) CrO_2 *or* Cr_5O_9.—The experimental value of χ compares favourably with the value of $36{\cdot}00 \times 10^{-6}$ (Börnstein's "Tabellen") for chromium dioxide. Further, the compound Cr_5O_9 has been described as being ferromagnetic (Honda and Sone, *Sci. Rep. Tohoku Imp. Univ.*, 1914, **3**, 223). Hence, the proper formula to be assigned to Dunnicliff's compound is CrO_2 and not Cr_5O_9.

Manchot and Kraus (*Ber.*, 1906, **39**, 3512) believed chromium in the dioxide to be quadrivalent although suggestions have been made that it may be bi-, ter-, or quadrivalent. It has been shown by Van Vleck ("Theory of Electric and Magnetic Susceptibilities," Oxford, particularly Chapter XI, p. 73), Sommerfeld ("Atombau," 4th Ed., p. 639), Bose (*Z. Physik*, 1927, **43**, 864), Stoner (*Phil. Mag.*, 1929, **8**, 250), and others that in the case of certain ions in which there is complete independence of *L*- and *S*-moments and hence the complete ineffectiveness of *L*-moment owing to interaction with neighbouring ions, the susceptibilities are given to a high degree of accuracy by the formula

$$\chi_M = N\beta^2[4s(s + 1)]/3kt \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

This relationship connects χ_M of ions with their valencies, for the value of the spin moment depends upon the valency of the ion in question. In the present case, the susceptibility value definitely supports the quadrivalency of chromium in the compound, as will be evident from the table below:

Constitutional formula		O:Cr·O·O·Cr:O	O:Cr:O
	(bivalent Cr).	(tervalent Cr).	(quadrivalent Cr).
Value of S, the spin moment	2	3/2	1
$\chi \times 10^6$ for chromium ion in different valency states, calc. from (1)	9996	6248	3332
Experimental value of $\chi_M \times 10^6$ after correction for oxygen	—	—	2955

(2) *Complex Chromium Sulphate.*—From the value of χ, the molecular susceptibility of the chromium ion was calculated, the necessary corrections being applied for the presence of other groups, *viz.*, $H_2O = -12\cdot90 \times 10^{-6}$ (International Critical Tables), $OH = -7\cdot54 \times 10^{-6}$ (Pascal), $SO_4 = -35\cdot60 \times 10^{-6}$ (International Critical Tables). It was thus found to be 6361×10^{-6} at 20°.

According to Hund (*Z. Physik*, 1925, **33**, 855), the effective Bohr magneton number can be calculated from the equation

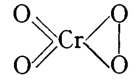
$$\mu_B = 2\cdot839\sqrt{\chi_M T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

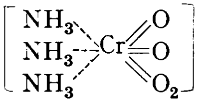
This gives us a value for $\mu_{\text{eff.}}$ of 3·898 Bohr magnetons, in close agreement with the theoretical deductions of Sommerfeld (*op. cit.*, p. 639), who calculated the magnetic moment in Bohr magnetons from the relationship $\mu_s = \sqrt{4s(s+1)}$, μ_s then being 3·88 Bohr magnetons for tervalent chromium.

Calculating χ_M on the basis of the Bose–Stoner formula and making the necessary corrections for the presence of other groups, we find the value of the specific susceptibility to be $34\cdot90 \times 10^{-6}$. Considering the nature of the compound, the agreement between the theoretical and the practical value is remarkable, and the magnetic data support the constitution assigned to it.

(3) *Triamminochromium Tetroxide.*—It has been postulated that chromium in the tetroxide may be sexavalent with a bivalent oxygen group (I). The triammino-tetroxide

(I.)

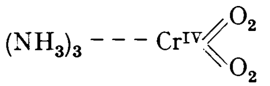


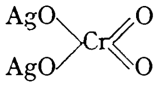


(II.)

can be formulated as (II), with the peroxidic oxygen occupying one position in the co-ordinate group (Werner, *Ber.*, 1906, **39**, 2659). The susceptibility determination, however, negatives the sexavalency of chromium in this compound, for if that were so the compound ought to have been diamagnetic or only feebly paramagnetic. Hence, we regard the compound as having the constitution (III), in which chromium is quadrivalent.

(III.)





(IV.)

The value of χ_M of this compound on the Bose–Stoner formula should be 3318×10^{-6}, and this compares fairly well with the experimental value of 3607×10^{-6}. As the latter is slightly higher than the former, it seems that the orbital moment is not fully quenched in this particular case. Illustrations of this type have been reported by Bhatnagar, Nevgi, and Khanna (*Phil. Mag.*, 1938, **25**, 234), Sucksmith (*Proc. Physical Soc.*, 1930, **42**, 388), and others. Moreover, the effective Bohr magneton number calculated from equation (2) yields a value of 2·94, and this is in agreement with the theoretical value of 2·83, calculated for quadrivalent chromium.

(4) *Silver Chromate.*—The diamagnetism of the compound clearly emphasises the sexavalency of chromium in it, and hence confirms the constitution (IV) assigned to it, which is analogous to the structure of chromic acid itself. It is to be particularly noted that the susceptibilities of the red and the green form are more or less identical. These colours have been attributed to different particle sizes, and the above observation

incidentally bears out the view that χ is independent of this (cf. Bhatnagar, Verma, and Haq, *Kolloid Z.*, 1937, **78**, 9; Lessheim, *Current Sci.*, 1936, **5**, 119).

(5) and (6) *Pyridinium and Quinolinium Tetrachlorohydroxychromate.*—If chromium in these compounds were quinquevalent, they would be strongly paramagnetic. The Bose–Stoner formula predicts a value of the order of 1250×10^{-6} for quinquevalent chromium. The experimental results, however, show that the former compound is only feebly paramagnetic, while the latter is diamagnetic. These results, therefore, indicate the sexavalency of chromium in these compounds, which may have the structure (V); this is not only capable of explaining the magnetic and the analytical results, but is also in agreement with the result of molecular-weight determinations, which show the compounds to be unimolecular. It will be noticed that this formula suggests the replacement of OH by bivalent O; this is not in disagreement with the analytical results, for they could scarcely detect the difference of one hydrogen atom.

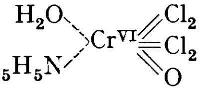
(7) *Dichloroaquotriamminochromic Chloride.*—The molecular susceptibility for chromium was calculated for the reddish-violet and the grey varieties. The effective Bohr magneton value was calculated from equation (2), and the results are shown below:

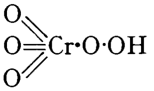
Modification.	$\chi_M \times 10^6$ for Cr.	$\mu_{eff.}$.
Reddish-violet	6724	3·98
Grey	6676	3·97

The corrections applied for the presence of other groups are: $NH_3 = -18{\cdot}7 \times 10^{-6}$ (International Critical Tables), $Cl' = -22{\cdot}2 \times 10^{-6}$ (Leiterer, *Z. physikal. Chem.*, 1937, *B*, **36**, 332), and H_2O as on p. 1432.

The effective Bohr magneton number in the two cases is in good accord with the theoretical value of 3·88 for tervalent chromium. It will also be observed that the χ values for the red and for the grey modification are very nearly the same, but the green salt has a markedly low value. In the last case, however, the salt was obtained only in hydrochloric acid solution, and as this may have introduced complications, this result is only tentative and of a qualitative nature.

When the solutions of the first two varieties were examined, the value of χ_s remained practically unchanged, but after the solution had been heated to boiling (whereupon the colour changed to green), there was a decided fall in the value of χ_s. This is an indication of a decomposition of the compound at this temperature. In all probability, this is merely a colloidal solution of chromium hydroxide which rapidly settles out.


(V.)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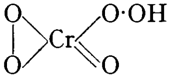
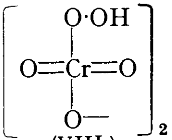

(VII.)

Magnetic measurements alone are therefore insufficient to fix the constitutions of these isomers, as the first two modifications have almost identical χ values, while the third is complicated by possible chemical factors.

Recourse was therefore also had to the study of absorption spectra of the three modifications (details will be communicated later). The close resemblance of the absorption curves for (i) the red solution of the grey variety and (ii) the red solution obtained from the reddish-violet variety by keeping its solution for 24 hours, suggested that the solution in both cases was formed by the development of the triaqua-salt (cf. Frowein, *loc. cit.*). The curves for the green isomer and the blue solution of the reddish-violet variety were of different shapes.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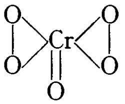
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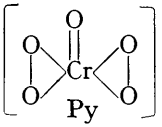
(X.)

(8) *Pyridine Salt of Perchromic Acid.*—It has been suggested (Riesenfeld, *Ber.*, 1908, **41**, 3946) that the compounds of the type $HCrO_5,X$, where X represents an organic base,

may be regarded as derivatives of an acid of the constitution (VI). Septavalent chromium, however, is not in harmony with the position of the metal in the periodic table, and it makes chromium an exception to the elements which form per-acids. The constitution (VII) or (VIII), in which chromium is quinque- or sexa-valent was therefore assigned to this compound. Schwarz and Giese (*loc. cit.*), who proposed the oxide formula for the compound, suggested the constitutions (IX) and (X) for the oxide and its pyridine derivative.

The magnetic results give a value of $+ 223{\cdot}66 \times 10^{-6}$ for molecular susceptibility, and after due allowance has been made for the presence of other groups, χ_M for chromium becomes $284{\cdot}60 \times 10^{-6}$. This value definitely negatives the quinquevalency of chromium required by (VII), for in that case χ_M for chromium would be 1229×10^{-6}. The formula (VIII) is probably incorrect, for, besides the chemical evidence adduced against it, Schwarz and Giese (*loc. cit.*) have shown that the compound is unimolecular in benzene, nitrobenzene, bromoform, and pyridine solutions.

This leaves the alternative constitution (X) for the pyridine compound, and this is in agreement with the magnetic results. The value of residual paramagnetism obtained is in accord with the very similar order of values ($170–330 \times 10^{-6}$) obtained by Tjabbes (*loc. cit.*) from a magnetic study of perchromates. Klemm and Werth (*Z. anorg. Chem.*, 1933, **216**, 127) arrived at a similar conclusion regarding the constitution of CrO_5,C_5H_5N, but as we have not access to their paper, we are unable to follow their reasoning.

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