**71.** *Polynuclear Compounds. Part I. Magnetic Properties of Some Binuclear Complexes.*

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The variation of magnetic susceptibility with temperature of a series of binuclear complexes of iron and chromium with one, two, and three bridging groups has been determined. The results have been used to determine the value of the exchange integral $(-J)$ between the magnetic ions. When the bridging groups are chlorine or the hydroxyl group only a small interaction is observed. However, in the case of the basic rhodo-complexes $[(NH_3)_5Cr \cdot O \cdot Cr(NH_3)_5]Br_4$ a marked magnetic interaction has been observed and this has been associated with the possibility of $\pi$-bonding between the chromium ions and the oxygen of the bridge. A similar type of interaction has been observed in the case of a phenanthroline–iron(III) complex. Additional evidence for $\pi$-bonding involving metal and oxygen has been obtained from a study of the infrared absorption spectra of the complexes.

THE study of the magnetochemistry of the transition elements has been mainly concerned with systems in which the interaction between the metal ions is considered to be negligible, *i.e.*, magnetically dilute compounds, and those in which the interaction may be considerable, *i.e.*, ferromagnetic and antiferromagnetic compounds. Polynuclear compounds are a valuable intermediate class and we are investigating the general interactions which occur in such compounds.

A binuclear compound can be considered as being formed by the combination of two mononuclear complex ions with one, two, three, or four bridging groups. If the interaction between the metal atoms is dependent on the distance between them, and no distortion is assumed to take place on formation of the complex, then the interaction will decrease in the order tetra- > tri- > di- > mono-bridged. If, however, the interaction is similar to that observed in many antiferromagnetic substances and requires the participation of the bridging group it will depend on the nature of this group and may also depend markedly on the M–L–M bond angle. We have investigated the magnetic interaction in a number of binuclear complexes of chromium and iron with a variation in the number and type of bridging groups.

### DISCUSSION

If we assume that the interaction between the two metal ions in a binuclear complex can be represented by the exchange integral, $-J$, then following the general procedure of Kambe [1] and Abragam and his co-workers [2] who calculated the susceptibilities of tri-nuclear complexes, the Hamiltonian for the system will be given by $H = -2J S_1 \cdot S_2$ where $S_1$ and $S_2$ are the spin vectors of the two ions.

The variation of the atomic susceptibility, $\chi_A$, with temperature for the metal will be given by the following equation [3] for the various values of $S = 5/2, 3/2, 1/2$:

$S = 5/2, 5/2$

$$\chi_A = \frac{3K}{T}\left[\frac{55 + 30\exp(10x) + 14\exp(18x) + 5\exp(24x) + \exp(28x)}{11 + 9\exp(10x) + 7\exp(18x) + 5\exp(24x) + 3\exp(28x) + \exp(30x)}\right] + N(\alpha)$$

$S = 3/2, 3/2$

$$\chi_A = \frac{K}{T}\left[\frac{42 + 15\exp(6x) + 3\exp(10x)}{7 + 5\exp(6x) + 3\exp(10x) + \exp(12x)}\right] + N(\alpha)$$

$S = 1/2, 1/2$

$$\chi_A = \frac{K}{T}\left[\frac{3}{3 + \exp(2x)}\right] + N(\alpha)$$

Where

$$K = g^2 N\beta^2/3k, \quad \chi = -J/kT,$$

[1] Kambe, *J. Phys. Soc. Japan*, 1950, **5**, 48.
[2] Yvon, Horrowitz, and Abragam, *Rev. Mod. Phys.*, 1953, **25**, 165.
[3] Earnshaw and Lewis, *Nature*, 1958, **181**, 1262.

and $g$ is the spectroscopic splitting factor, $\beta$ is the Bohr magneton, $k$ is Boltzmann's constant, $T$ is the temperature, and $N(\alpha)$ is the temperature-independent paramagnetic term.

The separation between the level specified by the quantum number $S^1$, and the ground level is given by $J\{S^1(S^1 + 1)\}$. Thus the singlet–triplet separation in a binuclear complex would be $2J$, and the triplet–quintet separation $4J$. Often the singlet–triplet separation is defined as $J$ (see ref. 4), so that the values of $J$ obtained differ by a factor of 2 from those given by this theory. The curve of $1/\chi$ against $T$ being considered for the case where $S = 3/2$, which is appropriate for spin-free, tervalent Cr (Fig. 1), the presence of an interaction $J$ would normally be detected by a finite value of $\theta$ in the Curie–Weiss equation, *i.e.*, $\chi = C/(T + \theta)$. As the value of $J$ increases, the deviation from a Curie plot becomes more marked and the value of $\theta$ increases. Magnetic interaction of the above type can be detected by the occurrence of an appreciable value of $\theta$, although this type of interaction

FIG. 1.
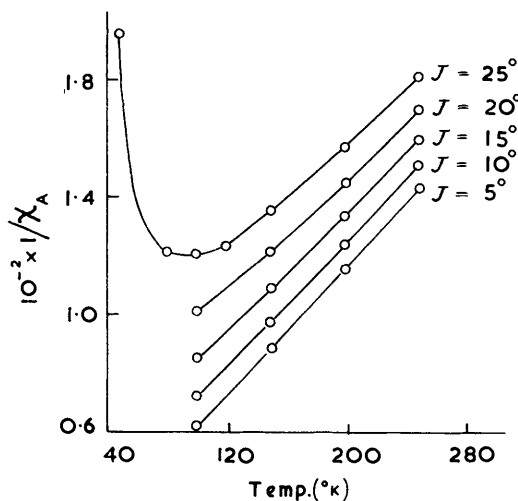


is only one of several possible causes for a significant value of $\theta$. It is also noticeable from these curves that a small value of the exchange integral $(-J)$ gives an appreciable value of $\theta$, and marked magnetic deviation occurs as the temperature approaches $J$, with the production of a minimum in the curve.

Very few magnetic measurements have been made on polynuclear compounds. Welo [5] carried out measurements on some trinuclear complexes of chromium and iron, and these were interpreted by Kambe [1] as indicating interactions of the order of $-14°$ for chromium and $-40°$ for iron. In the case of trinuclear complexes, the situation is complicated, for two different values of $J$ must be considered, corresponding to the interaction of the terminal atoms with the central atom and the two terminal atoms with each other. Recently, very precise data have been obtained for copper acetate and other copper salts of aliphatic carboxylic acids by Figgis and Martin [4] and Martin and Waterman; [6] the theory corresponding to $S = 1/2$ has been fully developed for these compounds. The data indicate that in these systems $J$ is of the order of $225°$, and the interaction has been considered to occur through the formation of a $\delta$-bond between the two copper atoms in the complexes. Wilmarth, Graff, and Gustin [7] reported measurements on the binuclear chromium complexes, termed the erythro- and rhodo-salts, and observed $\theta$ values of the order of $100°$, but did not attempt any theoretical interpretation of their results.

[4] Figgis and Martin, *J.*, 1956, 3837.
[5] Welo, *Phys. Rev.*, 1928, **32**, 320.
[6] Martin and Watermann, *J.*, 1957, 2545.
[7] Wilmarth, Graff, and Gustin, *J. Amer. Chem. Soc.*, 1956, **78**, 2683.

In addition to these measurements, there are the series of diamagnetic polynuclear complexes such as the metal carbonyl complexes where metal–metal bonding is considered to occur. These carbonyls correspond to polynuclear complexes in which the singlet–triplet separation is much greater than $kT$, with virtually complete occupation of the singlet level at room temperature. This form of magnetic behaviour would occur if the value of $J$ was of the order of $-1000°$.

In the case of the measurements we report, the compounds can be divided into three categories depending upon the number of bridging groups involved in the complexes.

(a) *Complexes with one bridging group.* An interesting series of binuclear chromium compounds containing a single bridging group are the erythro- and rhodo-series of salts. These complexes have recently been shown by Wilmarth

FIG. 2.

FIG. 3. $[(NH_3)_5Cr\cdot O\cdot Cr(NH_3)_5]Br_4$.
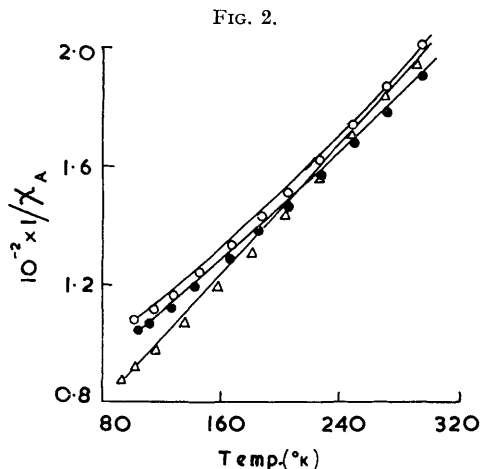


○ *Acid rhodo-bromide;* ● *acid erythro-bromide;* △ *basic erythro-bromide. Lines are calculated curves.*
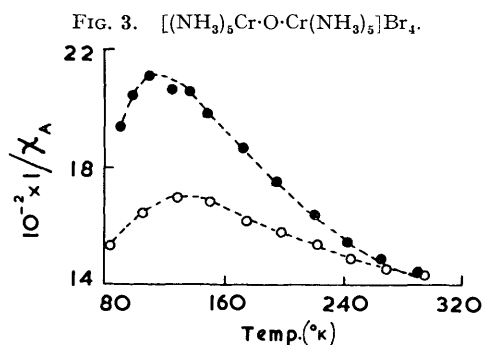
*et al.*[7] to be binuclear complexes involving hydroxy- and oxo-bridging groups, the acid erythro-series being $[(NH_3)_5Cr\cdot OH\cdot Cr(NH_3)_4(H_2O)]X_5$ and the acid rhodo-salts being $[(NH_3)_5Cr\cdot OH\cdot Cr(NH_3)_5]X_5$; the basic salts are formed by loss of a proton from the bridging hydroxyl group in the case of the rhodo-salts and from the aquo-group in the erythro-series. Thus the acid and basic erythro-salts and the acid rhodo-salts contain a hydroxyl-bridging group, whereas the basic rhodo-salt contains an oxo-bridging group.

For the acid and basic erythro- and acid rhodo-salts the plot of $1/\chi$ against $T$ is given in Fig. 2. The compounds show the typical behaviour of binuclear complexes, with a small value of the exchange integral. Table 1 contains the values of $J, g$, and $N(\alpha)$ required to give the theoretical curves. In the case of a low value of $J$, the theoretical plot is very sensitive to the value of $g$ used. There is a pronounced curvature of plot of $1/\chi$ against $T$, and the assignment of the $\theta$ can only be approximate. The value of $\mu_{eff.}$ changes from 3·5 B.M. at room temperature to a value of about 2·8 B.M. at 100° K (see Table 2). The values of $g$ observed are those to be expected for a chromium(III) complex, where $g$ is normally of the order of 2, since the $^4F$ term is split under a cubic crystal field into an orbital singlet lying lowest and two orbital triplets separated by an energy value much greater than $kT$.

In the case of the basic rhodo-salt, as noted by Wilmarth *et al.*[7] and Schäffer,[8] a considerable divergence from the behaviour of a mononuclear chromium salt is observed, the moment being reduced to 1·3 B.M. at room temperature. The moment, however,

[8] Schäffer, *J. Inorg. Nuclear Chem.,* 1958, **8**, 149.

falls sharply as the temperature is reduced (see Table 2). Fig. 3 gives typical results observed for this salt. The general magnetic behaviour was variable, depending upon the sample, a phenomenon also observed by Schäffer.[8] This probably arises from the

### TABLE 1.

| Compound | $\mu_{eff.}$ at 20° c (B.M.) | $J$ | $g$ | $N(\alpha) \times 10^6$ | $\theta$ |
|---|---|---|---|---|---|
| Acid rhodo-bromide ........................ | 3·44 | −20·25° | 1·94 | 62 | 120° |
| Acid erythro-bromide ..................... | 3·52 | −20·7 | 1·99 | 56 | 130 |
| Acid erythro-chloride ...................... | 3·62 | −20·7 | 1·99 | 56 | 130 |
| Basic erythro-bromide .................... | 3·50 | −14 | 1·91 | 56 | 70 |
| [pyH]$_5$[Cl$_5$Fe·Cl·FeCl$_5$] ................... | 5·57 | −1·5 | 1·92 | 0 | 12 |
| [(phen)$_2$Cr(OH)$_2$Cr(phen)$_2$]I$_4$,4H$_2$O ...... | 3·67 | −10 | 1·99 | 58 | 35 |
| [(gly)$_2$Cr(OH)$_2$Cr(gly)$_2$],H$_2$O ............... | 3·80 | −6 | 2·01 | 52 | 20 |
| [(phal)$_2$Cr(OH)$_2$Cr(phal)$_2$] ................... | 3·84 | −7 | 2·03 | 44 | 30 |
| [QH]$_4$[Cl$_4$FeCl$_2$FeCl$_4$] ........................ | 5·77 | −1·6 | 1·99 | 0 | 15 |
| [Et$_4$N]$_3$[Cl$_3$CrCl$_3$CrCl$_3$] ..................... | 3·94 | −5 | 2·08 | 46 | 12 |
| [pyH]$_3$[Cl$_3$FeCl$_3$FeCl$_3$] ..................... | 6·00 | −1·7 | 2·09 | 0 | 10 |

py = pyridine; phen = *o*-phenanthroline; gly = glycine; phal = phenylalanine; Q = quinoline

### TABLE 2. *Experimental atomic susceptibilities (c.g.s.) and magnetic moments (B.M.) at various temperatures.*

**Acid erythro-bromide**

| Temp. (κ) ...... | 293·7° | 268·4° | 246·6° | 224·0° | 201·5° | 182·6° | 162·5° | 139·4° | 122·8° | 107·3° | 100·4° |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $10^6\chi_A$ ............ | 5230 | 5590 | 5970 | 6380 | 6845 | 7240 | 7765 | 8430 | 8920 | 9360 | 9565 |
| $\mu_{eff.}$ ............... | 3·52 | 3·48 | 3·45 | 3·39 | 3·34 | 3·27 | 3·19 | 3·08 | 2·97 | 2·85 | 2·78 |

**Acid erythro-chloride**

| Temp. (κ) ...... | 290·8° | 269·8° | 248·0° | 223·9° | 200·4° | 174·0° | 149·4° | 115·5° | 101·2° |
|---|---|---|---|---|---|---|---|---|---|
| $10^6\chi_A$ ............ | 5510 | 5590 | 6000 | 6410 | 6960 | 7310 | 8240 | 9260 | 9660 |
| $\mu_{eff.}$ ............... | 3·60 | 3·49 | 3·46 | 3·40 | 3·36 | 3·20 | 3·15 | 2·94 | 2·81 |

**Basic erythro-bromide**

| Temp. (κ) ...... | 292·8° | 271·1° | 248·7° | 227·0° | 204·7° | 181·8° | 159·2° | 136·4° | 117·7° | 103·3° | 94·2° |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $10^6\chi_A$ ............ | 5174 | 5462 | 5907 | 6412 | 7017 | 7717 | 8447 | 9407 | 10,247 | 10,962 | 11,412 |
| $\mu_{eff.}$ ............... | 3·50 | 3·46 | 3·44 | 3·43 | 3·40 | 3·36 | 3·29 | 3·22 | 3·12 | 3·02 | 2·94 |

**Acid rhodo-bromide**

| Temp. (κ) ...... | 294·5° | 268·8° | 246·6° | 224·5° | 204·0° | 185·0° | 165·0° | 143·4° | 125·8° | 112·5° | 99·0° |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $10^6\chi_A$ ............ | 5230 | 5590 | 5970 | 6380 | 6845 | 7240 | 7765 | 8430 | 8920 | 9360 | 9565 |
| $\mu_{eff.}$ ............... | 3·44 | 3·41 | 3·38 | 3·35 | 3·31 | 3·24 | 3·17 | 3·07 | 2·94 | 2·85 | 2·73 |

**Basic rhodo-bromide**

| Temp. (κ) ...... | 294·7° | 266·9° | 244·6° | 222·2° | 196·6° | 173·9° | 150·1° | 138·1° | 126·3° | 111·8° | 99·4° |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $10^6\chi_A$ ............ | 702 | 676 | 652 | 611 | 572 | 535 | 503 | 484 | 484 | 472 | 488 |
| $\sigma_{eff.}$ ............... | 1·29 | 1·21 | 1·13 | 1·05 | 0·95 | 0·87 | 0·78 | 0·73 | 0·70 | 0·65 | 0·63 |
| Temp. (κ) ...... | 91·4° | 295·0° | 269·0° | 245·0° | 222·0° | 198·0° | 175·8° | 151·0° | 129·0° | 106·0° | 83·5° |
| $10^6X_A$ ............ | 515 | 703 | 692 | 681 | 652 | 637 | 622 | 596 | 591 | 608 | 652 |
| $\mu_{eff.}$ ............... | 0·62 | 1·29 | 1·23 | 1·16 | 1·08 | 1·01 | 0·94 | 0·85 | 0·78 | 0·78 | 0·66 |

**Pyridinium $\mu$-chloro-bis[pentachloroferrate(III)].**

| Temp. (κ) ...... | 295·5° | 250·2° | 221·4° | 178·4° | 144·6° | 106·0° | 79·5° |
|---|---|---|---|---|---|---|---|
| $10^6\chi_A$ ............ | 13,070 | 15,260 | 17,240 | 21,050 | 25,720 | 33,710 | 44,450 |
| $\mu_{eff.}$ ............... | 5·58 | 5·55 | 5·55 | 5·50 | 5·48 | 5·37 | 5·34 |

**Di-$\mu$-hydroxy-bis[di-*o*-phenanthrolinechromium(III)] iodide tetrahydrate**

| Temp. (κ) ...... | 292·0° | 274·8° | 261·1° | 246·2° | 232·5° | 215·4° | 207·2° | 196·2° | 178·5° | 168·0° | 159·4° |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $10^6\chi_A$ ............ | 5720 | 6030 | 6330 | 6690 | 7000 | 7410 | 7760 | 8090 | 8770 | 9240 | 9600 |
| $\mu_{eff.}$ ............... | 3·67 | 3·66 | 3·65 | 3·64 | 3·62 | 3·59 | 3·60 | 3·58 | 3·55 | 3·54 | 3·51 |
| Temp. (κ) ...... | 152·8° | 143·5° | 135·5° | 126·0° | 120·5° | 109·8° | 101·8° | 93·5° | | | |
| $10^6\chi_A$ ............ | 9940 | 10,400 | 11,000 | 11,600 | 12,190 | 13,000 | 13,700 | 14,810 | | | |
| $u_{eff.}$ ............... | 3·50 | 3·47 | 3·47 | 3·43 | 3·44 | 3·39 | 3·35 | 3·34 | | | |

**Di-$\mu$-hydroxy-bis[di(glycine)chromium(III)] monohydrate**

| Temp. (κ) ...... | 306·3° | 296·7° | 274·8° | 252·2° | 228·2° | 205·1° | 188·5° | 159·0° |
|---|---|---|---|---|---|---|---|---|
| $10^6\chi_A$ ............ | 5780 | 6080 | 6440 | 7030 | 7750 | 8570 | 9290 | 10,750 |
| $\mu_{eff.}$ ............ | 3·78 | 3·81 | 3·78 | 3·78 | 3·78 | 3·77 | 3·76 | 3·71 |
| Temp. (κ) ...... | 141·0° | 117·8° | 98·4° | 88·0° | | | | |
| $10^6\chi_A$ ............ | 11,960 | 14,000 | 16,080 | 17,310 | | | | |
| $\mu_{eff}$ ............ | 3·69 | 3·65 | 3·57 | 3·51 | | | | |

TABLE 2. *(Continued.)*

### Di-μ-hydroxybis[di(phenylalanine)chromium(III)]

| Temp. (K) | 297·6° | 285·0° | 270·6° | 253·3° | 241·1° | 224·9° | 210·4° | 195·4° |
|---|---|---|---|---|---|---|---|---|
| $10^6\chi_A$ | 6160 | 6320 | 6650 | 7060 | 7400 | 7890 | 8470 | 9020 |
| $\mu_{eff.}$ | 3·85 | 3·81 | 3·81 | 3·80 | 3·79 | 3·78 | 3·79 | 3·77 |
| Temp. (K) | 181·6° | 165·2° | 150·8° | 134·4° | 118·6° | 103·6° | 89·0° | |
| $10^6\chi_A$ | 9580 | 10,380 | 11,210 | 12,580 | 13,490 | 15,000 | 17,000 | |
| $\sigma_{eff.}$ | 3·75 | 3·72 | 3·69 | 3·69 | 3·59 | 3·54 | 3·34 | |

### Quinolinium di-μ-chlorobis[tetrachloroferrate(III)]

| Temp. (K) | 294·6° | 255·3° | 207·8° | 169·4° | 106·0° |
|---|---|---|---|---|---|
| $10^6\chi_A$ | 14,030 | 16,250 | 20,000 | 24,030 | 35,370 |
| $\mu_{eff.}$ | 5·78 | 5·78 | 5·79 | 5·73 | 5·50 |

### Tetraethylammonium tri-μ-chlorobis[trichlorochromate(III)]

| Temp. (K) | 296·5° | 281·4° | 265·6° | 244·5° | 219·4° | 196·3° | 175·8° | 152·6° | 134·0° | 115·0° | 112·4° |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $10^6\chi_A$ | 6550 | 6820 | 7200 | 7850 | 8700 | 9740 | 10,800 | 12,290 | 13,780 | 15,310 | 15,780 |
| $\mu_{eff.}$ | 3·96 | 3·93 | 3·93 | 3·93 | 3·92 | 3·92 | 3·91 | 3·89 | 3·86 | 3·86 | 3·77 |
| Temp. (K) | 98·0° | 88·8° | 80·0° | | | | | | | | |
| $10^6\chi_A$ | 17,620 | 18,950 | 20,290 | | | | | | | | |
| $\mu_{eff.}$ | 3·73 | 3·68 | 3·62 | | | | | | | | |

### Pyridinium tri-μ-chlorobis[trichloroferrate(III)]

| Temp. (K) | 295·8° | 284·1° | 261·5° | 238·3° | 218·7° | 199·0° | 180·0° | 162·0° | 145·0° |
|---|---|---|---|---|---|---|---|---|---|
| $10^6\chi_A$ | 15,130 | 15,580 | 17,150 | 18,760 | 20,550 | 22,690 | 24,420 | 26,900 | 30,180 |
| $\mu_{eff.}$ | 6·01 | 5·98 | 6·01 | 6·00 | 6·02 | 6·03 | 5·96 | 5·93 | 5·94 |
| Temp. (K) | 128·5° | 111·1° | 99·0° | 93·3° | | | | | |
| $10^6\chi_A$ | 34,100 | 38,410 | 42,770 | 44,520 | | | | | |
| $\mu_{eff.}$ | 5·94 | 5·87 | 5·84 | 5·79 | | | | | |

### Iron(III)–phenanthroline chloride complex

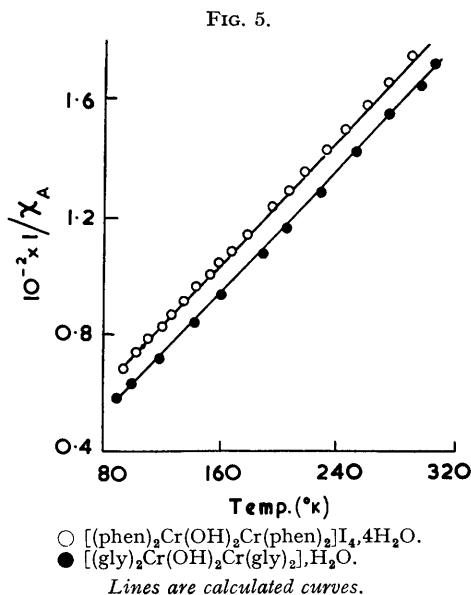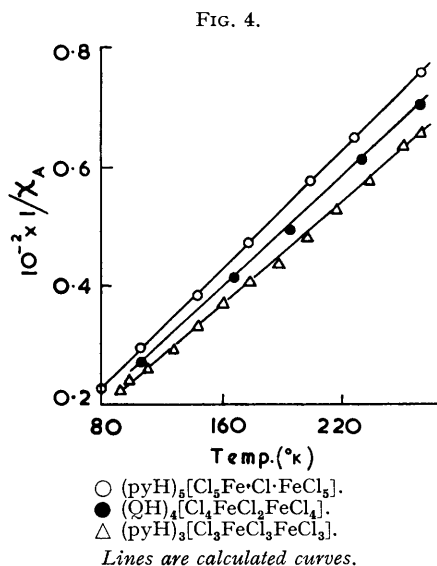| Temp. (K) | 356·6° | 346·4° | 333·0° | 316·5° | 279·0° | 253·5° | 229·2° | 208·8° | 187·0° |
|---|---|---|---|---|---|---|---|---|---|
| $10^6\chi_A$ | 1427 | 1419 | 1392 | 1381 | 1381 | 1358 | 1336 | 1305 | 1259 |
| $\mu_{eff.}$ | 2·03 | 1·99 | 1·93 | 1·88 | 1·76 | 1·67 | 1·57 | 1·48 | 1·38 |
| Temp. (K) | 161·8° | 139·0° | 117·5° | 105·5° | 98·3° | 95·7° | 90·1° | | |
| $10^6\chi_A$ | 1183 | 1092 | 981 | 909 | 871 | 821 | 814 | | |
| $\mu_{eff.}$ | 1·25 | 1·11 | 0·96 | 0·88 | 0·83 | 0·80 | 0·77 | | |

presence of a small concentration of the basic erythro-salt which analytically would be difficult to detect. As the temperature is lowered the susceptibility of the erythro-salt rises, and at 100° $\chi_A$ is of the order of 10,000 × $10^{-6}$ c.g.s., so that the presence of a small percentage of this complex would have a marked effect on the susceptibility over the lower temperature range; the differences in susceptibility noted in Fig. 3 could arise from the presence of about 1% of the erythro-salt. We have attempted to remove this impurity by sealing samples of the basic rhodo-bromide in tubes with liquid ammonia for periods of up to two days, but the susceptibility of the sample did not change on this treatment.

Schäffer noted a marked difference between the ultraviolet spectra of the basic rhodo-complex and the acid rhodo- and erythro-complexes, and has suggested, as also have Wilmarth *et al.*,[7] that the large reduction in magnetic behaviour may be associated with the presence of π-bonding between the chromium ions and the oxygen in the bridge. This is essentially the explanation used by Dunitz and Orgel [9] to account for the diamagnetism of the chloro-ruthenium complex $K_4[Ru_2OCl_{10}],H_2O$. In the case of the basic erythro-salt in addition to this π-bonding mechanism there must be a further interaction leading to the reduction in moment, as the direct application of Dunitz and Orgel's theory gives a moment corresponding to one unpaired electron per chromium atom. The order of energy levels in the case of the ruthenium–oxygen system was given as $[Eu^b][(B_{2g})(B_{2u})(E_g)][Eu^a]$. For the ten electrons of the chromium–oxygen system (three from each chromium atom and four from the oxygen), the non-bonding $E_g$ orbital would be thus doubly occupied, with the resultant moment of one unpaired electron per chromium.

[9] Dunitz and Orgel, *J.*, 1953, 2594.

This behaviour is similar to that observed [10] for some binuclear oxy-bridging complexes of rhenium(IV) containing the ion $[Re_2OCl_{10}]^{4-}$. These compounds were found to be diamagnetic, whereas a moment corresponding to one unpaired electron might have been expected. In agreement with the suggested $\pi$-bonding between the oxygen and the chromium ions, we have observed the appearance of bands in the infrared absorption spectra at 854 and 870 cm.$^{-1}$. This is in the absorption range that has been found for systems containing oxygen double-bonded to metals.[11]

The basic rhodo-salt is thus an example of interaction occurring through an intermediate ligand group, as occurs in the super-exchange mechanism suggested to explain interaction in antiferromagnetic compounds.[12] The smaller interaction observed in the erythro- and acid rhodo-salts may be associated with a metal–oxygen–metal bond angle of the order of 120°, rather than 180° as may occur in the basic rhodo-salt. The linear system leads to a much more favourable interaction, for when the oxygen uses $sp$ hybrid



Fig. 4.

○ $(pyH)_5[Cl_5Fe \cdot Cl \cdot FeCl_5]$.
● $(QH)_4[Cl_4FeCl_2FeCl_4]$.
△ $(pyH)_3[Cl_3FeCl_3FeCl_3]$.
*Lines are calculated curves.*



Fig. 5.

○ $[(phen)_2Cr(OH)_2Cr(phen)_2]I_4,4H_2O$.
● $[(gly)_2Cr(OH)_2Cr(gly)_2],H_2O$.
*Lines are calculated curves.*

bonds to form a $\sigma$-bond to the metal, the remaining $p$ orbitals may form a $\pi$-bonding system with the metal $d_{xy}$, $d_{yz}$, or $d_{xz}$ orbitals. There is, however, the possibility that, in the case of the basic rhodo-salt, the complex may contain more than two chromium atoms per molecule, as no direct molecular-weight determinations have been made owing to the insolubility of the salts. In this case the interaction may take place over a number of metal–oxygen bonds. With the acid erythro- and rhodo-salts determinations of the molecular weight from $X$-ray measurements have shown them to be binuclear complexes.

The remaining single-bridging complex investigated was the chloro-bridged iron compound $(pyH)_5[Cl_5Fe \cdot Cl \cdot FeCl_5]$, where py = pyridine. The plot of $1/\chi$ against $T$ is given in Fig. 4, and the theoretical curve corresponded to $J = -1 \cdot 5°$, $g = 1 \cdot 92$, $N(\alpha) = 0$. The pyridine in this complex has been shown from infrared measurements, to be all present as pyridinium ion, as the characteristic absorption appearing in the 1450 cm.$^{-1}$ region which occurs when pyridine is co-ordinated to a metal ion [13] is absent in this complex.

[10] Jezowska-Trzebiatowska and Wajda, *Bull. Acad. polon. Sci.*, Cl. III, 1954, **2**, 249.
[11] Barraclough, Lewis, and Nyholm, *J.*, 1959, 3552.
[12] Lidiard, *Rep. Progr. Phys.*, 1954, **17**, 201.
[13] Sharp, personal communication.

In the case of ferric complexes, the effect of a given value of $-J$ on the magnetic properties will be more marked than with chromium complexes, as the separation of the ground level, $S = 0$, to the highest level, $S = 3$ in the case of chromium and $S = 5$ in that of iron, will be $12J$ and $30J$ respectively.

(b) *Complexes with two bridging groups.* Four compounds that definitely fall into this class have been investigated. They are the dihydroxychromium complexes with glycine, phenylalanine, and phenanthroline as the other ligands, and a di-chloro-bridged iron complex. The plots of $1/\chi$ against $T$ (Figs. 4, 5, and 6) all suggest slight interaction in the systems, and the $J$, $g$, and $N(\alpha)$ values for the theoretical curves are given in Table 1. The susceptibilities are very little different from those of the free-ion value at room temperature, but fall below this value at lower temperatures. However, all the lines show a slight curvature which can normally only be detected by determining a sufficient number of points on the graph. The $g$ values obtained are very close to 2, indicating the
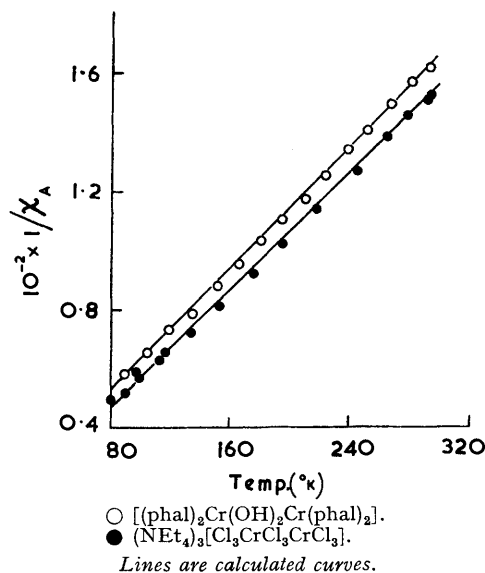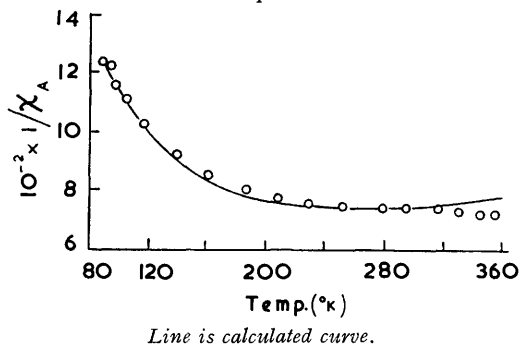


Fig. 6.

O [(phal)$_2$Cr(OH)$_2$Cr(phal)$_2$].
● (NEt$_4$)$_3$[Cl$_3$CrCl$_3$CrCl$_3$].
*Lines are calculated curves.*

Fig. 7. *Iron(III)–phenanthroline chloride tetrahydrate complex.*

*Line is calculated curve.*

absence of any appreciable orbital contribution to the moment, as would be expected for chromium(III) and spin-free iron(III) complexes.

A complex that can be considered formally to be of this class is the phenanthroline–iron compound obtained on adding phenanthroline to ferric chloride solutions. This has been given [14] the structure [(phen)$_2$Fe(OH)$_2$Fe(phen)$_2$]Cl$_4$. The plot of $1/\chi$ against $T$ is given in Fig. 7, and a considerable reduction in moment occurs at low temperatures. The general characteristics of the curve can be reproduced if it is assumed that the complex is a spin-paired iron(III) compound with $J = 200°$, $N(\alpha) = 628$, and $g = 1.97$ (full line in Fig. 7). If the compound is a binuclear complex with an oxygen bridge, as suggested for the basic rhodo-salts, then the high value of $J$ may be accounted for on a similar $\pi$-bonding mechanism. The moment per iron atom would then correspond to one unpaired electron, the two unpaired electrons of the iron atoms occupying the anti-bonding [$Eu^a$] orbital, so the reduction in moment below this value at lower temperatures involves a further interaction between the two electrons, as occurs with the chromium and rhenium complexes discussed above. Such a complex would involve an asymmetric ligand field,

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[14] Gaines, Hammett, and Walden, *J. Amer. Chem. Soc.*, 1936, **58**, 1668.

and the $T_{2g}$ orbital of the iron would be split into a lower singlet and upper doublet. The high value for the temperature-independent paramagnetic term may then arise from the presence of this upper doublet level. However, it is difficult to reconcile this mechanism with a $g$ value of 1·97, as such a mechanism should lead to an aniosotropic $g$ of average value of the order of 2·3. The problem in the case of this complex is complicated by the fact that the singlet–triplet separation is of the order of the spin–orbit coupling [Fe(III) = 440 cm.$^{-1}$], and calculations are being carried out by Dr. Figgis on this system with a simultaneous perturbation by spin–orbit coupling and exchange interaction. However, the infrared spectrum of this compound, as that of the basic rhodo-complex, shows in addition to the normal bonds observed in phenanthroline complexes, strong absorption in the region expected for metal–oxygen double bonds (852 cm.$^{-1}$). The presence of an oxygen bridge would also require the formulation of the complex as [(phen)$_2$(H$_2$O)Fe–O–FeCl(phen)$_2$]Cl$_2$ with the presence of at least one chloride ion in the co-ordination sphere of the metal, in the case of the anhydrous salt, in order to maintain the iron co-ordination number at 6. It is noteworthy that all attempts to prepare derivatives of the complex by replacement of the chloride with other anions have so far failed; this can be understood if the anions take part in the co-ordination sphere.

The iron complex behaves completely differently from the corresponding chromium complex, which appears from molecular-weight determinations to be the dimer [(phen)$_2$Cr(OH)$_2$Cr(phen)$_2$]I$_4$. As with the rhodo-complex no molecular-weight determinations have been made on the iron–phenanthroline complex, and this may be a poly-nuclear system containing a number of metal–oxygen bridging systems.

(c) *Complexes with three bridging groups.* The $\mu$, $\mu^{\mathrm{I}}$, $\mu^{\mathrm{II}}$-trichloro-complexes of chromium(III) and iron(III), [Cl$_3$MCl$_3$MCl$_3$]$^{3-}$, have been investigated. The plots of $1/\chi$ against $T$ are given in Figs. 4 and 5, and the values of $J$, $g$, and $N(\alpha)$ corresponding to the theoretical curves are given in Table 1. The interaction in both cases is extremely small. The X-ray structure of the cæsium salt of the chromium complex indicates that the chromium octahedra are distorted on formation of the binuclear complex in such a way that the chromium ions move apart [15]; the iron complex ion probably has a similar structure, as the cæsium salts have been shown by X-ray measurements to be isomorphous. The behaviour of the chromium compound is in sharp contrast to that of the corresponding tungsten complex ion [W$_2$Cl$_9$]$^{3-}$, where the X-ray data indicate a very short tungsten–tungsten distance.[16] In this complex the resultant diamagnetism can be explained by the formation of a direct tungsten–tungsten bond.

The results obtained for this series of compounds imply that the major interaction occurs when a bridging group such as oxygen is present, for then a $\pi$-bonding mechanism can operate between the metal–ligand–metal system. In the case of hydroxyl and chloride ions, the interaction is very much smaller, and may then occur by the delocalisation of elec-trons from the metal ion into anti-bonding orbitals of the bridging group. In the chromium compounds, the interaction appears to decrease with increasing multiplicity of the bridging groups, although it has not been possible to investigate a series involving the same bridging group.

## EXPERIMENTAL

The erythro- and rhodo-compounds were prepared as described by Jörgensen [17] and by Wilmarth *et al.*[7]

The analyses of the compounds were as follows: they are best characterised by their nitrogen analyses. Acid rhodo-bromide (Found: N, 20·3; Cr, 15·2; Br, 58·0. Calc. for H$_{31}$Br$_5$Cr$_2$N$_{10}$O: N, 20·3; Cr, 15·05; Br, 57·85%). Basic rhodo-bromide (Found: N, 23·2; Cr, 16·9; Br, 52·6. Calc. for H$_{30}$Br$_4$Cr$_2$N$_{10}$O: N, 22·95; Cr, 17·05; Br, 52·4%). Acid

[15] Wessel and Ijdo, *Acta Cryst.*, 1957, **10**, 466.
[16] Watson and Waser, *Acta Cryst.*, 1958, **11**, 689.
[17] Jörgensen, *J. prakt. Chem.*, 1882, **25**, 398.

erythro-chloride (Found: N, 26·7; Cr, 22·3; Cl, 37·9. Calc. for $H_{30}Cl_5Cr_2N_9O_2$: N, 26·8; Cr, 22·1; Cl, 37·75%). Acid erythro-bromide (Found: N, 18·8; Cr, 14·7; Br, 57·4. Calc. for $H_{30}Br_5Cr_2N_9O_2$: N, 18·25; Cr, 15·0; Br, 57·8%). Basic erythro-bromide (Found: N, 20·8; Cr, 16·7; Br, 51·9. Calc. for $H_{29}Br_4Cr_2N_9O_2$: N, 20·6; Cr, 17·0; Br, 52·3%).

*Di-μ-hydroxybis[di-o-phenanthrolinechromium(III)] iodide tetrahydrate.* This was prepared by Dwyer's method [18] (Found: C, 40·1; H, 3·1; N, 7·5%; *M*, cryoscopically in 0·7% aqueous solution, 297. Calc. for $C_{48}H_{42}Cr_2I_4N_8O_6$: C, 40·1; H, 2·9; N, 7·8%.

*Di-μ-hydroxybis[di(glycine)chromium(III)] monohydrate.* An aqueous solution (70 ml.) of chromic chloride (13·3 g.) and glycine (11·3 g.) was treated with an aqueous solution (20 ml.) of sodium hydroxide (6 g.). The pink precipitate was washed thoroughly with alcohol [19] (Found: C, 12·6; H, 4·6; N, 12·3. Calc. for $C_8H_{20}CrN_4O_{11}$: C, 21·25; H, 4·5; N, 12·4%).

*Di-μ-hydroxybis[di(phenylalanine)chromium(III)].* Phenylalanine (6 g.) was refluxed with an aqueous solution (250 ml.) of tris(ethylenediamine)chromium(III) chloride (5 g.) [20] (Found: C, 54·9; H, 5·9; N, 7·3; Cr, 13·4. Calc. for $C_{36}H_{42}Cr_2N_4O_{10}$: C, 54·4; H, 5·3; N, 7·05; Cr, 13·1%).

*Tristetraethylammonium tri-μ-chloro-bis[trichlorochromate(III)].* Saturated solutions of tetraethylammonium chloride (3·2 g.) and chromic chloride (1·1 g.) in methyl cyanide were mixed, and the solution was allowed to crystallise. The crystals were dried under vacuum at 100° to remove methyl cyanide [21] (Found: C, 35·5; H, 7·5; N, 7·2; Cl, 39·0; Cr, 12·8. Calc. for $C_{24}H_{60}Cl_9Cr_2N_3$: C, 35·4; H, 7·4; N, 5·2; Cl, 39·2; Cr, 12·8%).

*Tripyridinium tri-μ-chlorobis[trichloroferrate(III)].* Ferric chloride (27 g.), pyridine (12 g.), and hydrochloric acid (13 ml.) were mixed, and the precipitate was recrystallised from methylated spirits [22] (Found: C, 27·2; H, 2·65; N, 6·1; Cl, 47·65; Fe, 16·4. Calc. for $C_{15}H_{18}Cl_9Fe_2N_3$: C, 26·85; H, 2·7; N, 6·3; Cl, 47·5; Fe, 16·6%).

*Pentapyridinium μ-chlorobis[pentachloroferrate(III)].* Tripyridinium tri-μ-chlorobis[trichloroferrate(III)] (1 g.) was mixed with pyridine hydrochloride (2·4 g.) in alcohol (12 ml.). The compound slowly crystallised from the solution [22] (Found: C, 33·75; H, 3·4; N, 7·55. Calc. for $C_{25}H_{30}Cl_{11}Fe_2N_5$: C, 33·25; H, 3·35; N, 7·8%).

*Tetraquinolinium di-μ-chlorobis[tetrachloroferrate(III)].* Quinolinium chloride (2·6 g.) was added to a solution of ferric chloride hexahydrate (2·7 g.) in concentrated hydrochloric acid (30 ml.) [22] (Found: C, 43·5; H, 3·0; N, 5·7; Cl, 35·5; Fe, 11·4. Calc. for $C_{36}H_{32}Cl_{10}Fe_2N_4$: C, 43·8; H, 3·3; N, 5·7; Cl, 35·9; Fe, 11·3%).

*Iron(III)–phenanthroline chloride tetrahydrate complex.* This substance separated from a suspension of o-phenanthroline in aqueous ferric chloride solution, as described by Hammett *et al.* [14] (Found: C, 53·25; H, 4·1; Fe, 10·5. Calc. for $C_{48}H_{42}Cl_4Fe_2N_8O_6$: C, 53·35; H, 3·9; Fe, 10·3%). The anhydrous compound also was analysed for iron (Found: Fe, 11·25. Calc. for $C_{48}H_{34}Cl_4Fe_2N_8O_2$: Fe, 11·1%).

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[20] Bailar, Stiegman, Balthis, and Huffmann, *J. Amer. Chem. Soc.*, 1939, **61**, 2402.
[21] Machin, personal communication.
[22] Weinland and Kissling, *Z. anorg. Chem.*, 1922, **120**, 209.