Exchange Reactions and Magnetic Susceptibilities of Complex Salts. Part I. Some Complex Salts of Ferric Iron.

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The following magnetic moments (Bohr magnetons) have been found for the potassium salts : ferrioxalate ($+2H_2O$) 5·88, (anhyd.) 5·92, ferrimalonate ($+H_2O$) 5·87, and ferricyanide 2·50. Molecular field constants are zero, except for the ferricyanide for which it is $-43°$. The oxalate and malonate salts showed rapid exchange with ^{14}C-labelled ligand ions. The ferricyanide showed exchange only at high acidities.

The significance of magnetic susceptibility as a criterion of the nature of metal–ligand bonds in complex salts has often been discussed (*e.g.*, Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, 1945, p. 37; *J.*, 1948, **1461**). The sharply alternative modes of spin coupling which lead to high and low values for the susceptibility with the exclusion of intermediate values are of particular interest (Pauling, *op. cit.*, p. 117). In general, experiments with labelled ligand ions showed instantaneous exchange for " ionic " (highly paramagnetic) complex salts and very little for " covalent " complex salts (salts showing diamagnetism or small paramagnetism; Long, *J. Amer. Chem. Soc.*, 1941, **63**, 1353; Adamson, Welker, and Wright, *ibid.*, 1951, **73**, 4786). In the present work the magnetic susceptibilities of potassium ferrioxalate and ferrimalonate are compared with their exchange reactions with labelled ligand ions; higher members of the series were too unstable in solution for such work. Potassium ferricyanide was included as an example of a " covalent " complex salt.

Experimental

Magnetic susceptibilities were determined on a Gouy-type magnetic balance, the current through the electromagnet being regulated within 0·002%. (The regulator will be described elsewhere.)

Susceptibility measurements were made at 297·48°, 198·0°, and 90·1° K, with water in a thermostat, solid carbon dioxide–acetone, and liquid oxygen respectively.

Calibration was effected with solutions of nickel chloride (Nettleton and Sugden, *Proc. Roy. Soc.*, 1939, *A*, **173**, 313) and copper sulphate (de Haas and Gorter, *Proc. Acad. Sci., Amsterdam*, 1930, **33**, 1101) at 297·48° K, and powdered ferrous ammonium sulphate and copper sulphate pentahydrate at 198·0° and 90·1° K.

At each temperature agreement within 0·3% between the standards was obtained. Corrections for diamagnetism were made, Pascal's constants being used.

Tracer experiments were performed with ^{14}C-labelled ligands prepared from materials supplied by A.E.R.E., Harwell. Activity determinations were made on infinitely thick samples (prepared by filtration on to filter paper in a stainless-steel Buchner-type funnel), with an end-window G.M. counter mounted within a lead castle. All activities were counted for sufficient time to bring the probable error below 2%; the background count of about 15 counts per minute was determined at the time of each counting and was subtracted.

Potassium Ferrioxalate.—The green potassium ferrioxalate was precipitated by the addition of ethyl alcohol to a mixture of concentrated aqueous solutions of ferric chloride and potassium oxalate, and then recrystallised from aqueous alcohol. Although the reported photochemical decomposition was too slow to affect any of the results, the compound was stored in the dark. The green crystals were dried in a desiccator and then at 110° for 3 hr. [loss in wt., 8·0. Calc. for $K_3Fe(C_2O_4)_3,2H_2O$: H_2O, 7·6%].

The anhydrous material was analysed for iron and oxalate, by titration with standard permanganate, followed by reduction with amalgamated zinc in a Jones reductor and titration again with permanganate [Found: Fe, 12·7; C_2O_4, 60·3. Calc. for $K_3Fe(C_2O_4)_3$: Fe, 12·8; C_2O_4, 60·4%].

The magnetic-susceptibility values (c.g.s. units $\times 10^6$/g.) are tabulated.

Temp. (K)	χ_g. Anhyd.	χ_g. Hydrated	χ_M	χ_M (corr.)	$10^4/\chi_{M\,corr.}$
297·48°	32·70 ± 0·03	29·68 ± 0·05	14,130	14,363	0·6964
198·0	48·34 ± 0·06	44·91 ± 0·14	21,485	21,718	0·4603
90·1	105·68 ± 0·13	98·02 ± 0·24	46,860	47,093	0·2124

A plot of $1/\chi_{M.\,corr.}$ against *T* gave a straight line through the origin, *i.e.*, the molecular field constant (Δ) is 0, and hence the magnetic moment is 5·88 Bohr magnetons (cf. Jackson, *Proc. Roy. Soc.*, 1933, *A*, **140**, 695), this being within 1% of the moment (5·92 B.M.) expected for 5 unpaired spins if orbital contributions are neglected.

Exchange experiments. Sodium [^{14}C]oxalate was prepared by heating sodium [^{14}C]formate. An aqueous solution was prepared containing 0·050 mole/l. of active sodium oxalate and 0·070 mole/l. of potassium ferrioxalate, which were then separated by addition of a slight excess of barium nitrate solution; this precipitated the "free" oxalate, leaving the "complexed" oxalate in solution. The precipitate was filtered off, providing counting samples (*a*). Silver nitrate solution was added to the filtrate which was then boiled, causing a slow and incomplete precipitation of the "complexed" oxalate as silver oxalate (samples *b*). The activities expected if no exchange had occurred were determined as follows. The oxalate from an aliquot sample of sodium oxalate solution was precipitated as barium oxalate [counting samples (*c*)]. An aliquot sample of the solution of potassium ferrioxalate was then added to the filtrate, and a silver oxalate sample (*d*) prepared from the resultant solution as before. Any activity in this sample was attributed to the presence of traces of active sodium oxalate in the filtrate, or to unconverted formate. For complete exchange the activity of the "free" oxalate should have

Exchange time (hr.)	Activity (counts/min.) of :			
	Ba oxalate (*a*)	Ag oxalate (*b*)	Samples (*c*)	Samples (*d*)
0	188, 180	152, —	424	6
1	181	137	404	17
2	169	124	385	12
26	—	172	Mean 405	Mean 12
	Mean 180	Mean 142		

Corrected mean : 142 − 12 = 130.

been reduced in the ratio of the concentrations of the constituents of the solution, *i.e.*, 5 : (5 + 7). Therefore, the expected number of counts per minute for equilibrium = 405 × 5/12 = 170. The observed value was 180. Expressing the values as relative activites per mole of oxalate we have: "complexed" oxalate 130 counts/g./min. ≡ 400 counts/equiv./min.; and "free" oxalate 180 counts/g./min. ≡ 405 counts/equiv./min. *I.e.*, exchange proceeds to equilibrium in the few seconds necessary for the separation.

Potassium Ferrimalonate.—Concentrated aqueous solutions of ferric chloride (1 mol.), potassium hydroxide (6 mols.), and malonic acid (3 mols.) were mixed at 50°. The resulting solution deposited a green oil which crystallised rapidly. The crystals were fairly soluble in water, but the aqueous solution was not very stable, becoming brown in 1—2 hr. in the cold. The salts was analysed by a modification of Durand's permanganate method (*Ann. Chim. analyt.*, 1903, **8**, 330), addition of excess of 0·1N-permanganate, storage for 1½ hr. at 70°, and back-titration with standard potassium tetroxalate, and iron was determined as for potassium ferrioxalate (Found: Fe, 11·2; malonate, 61·3. Calc. for $C_3H_2O_4FeK_3,H_2O$: Fe, 11·2; malonate, 61·5%). The fact that both values are slightly low is ascribed to a trace of water in the salt since the iron : malonate ratio is 1 : 3·001.

The magnetic-susceptibility values (c.g.s. units $\times 10^6$/g.) are tabulated.

Temp. (K)	χ_g.	χ_M.	χ_M. (corr.)	$10^4/\chi_{M.\ corr.}$
297·5°	28·42	14,120	14,340	0·6975
198·0	43·18	21,455	21,675	0·4602
90·1	91·60	45,510	45,760	0·2185

A plot of $1/\chi_{M.\ corr.}$ against T gives a straight line through the origin, *i.e.*, $\Delta = 0$, and hence the magnetic moment is 5·87 B.M.

Exchange experiments. Potassium [α-^{14}C]malonate was prepared by refluxing ethyl malonate with an excess of aqueous potassium hydroxide and final neutralisation with malonic acid. An aqueous solution was prepared containing 0·11 mole/l. of active potassium malonate and 0·14 mole/l. of potassium ferrimalonate. Separation was effected by addition of barium chloride solution immediately after mixing; the "free" malonate was precipitated slowly, during 0·5 hr. The precipitate was filtered off and its activity determined:

Ba malonate activities (counts/min.). Without complex salt: 1167, 1132, 1261; mean, 1187. With complex salt: 701, 734, 731; mean, 722.

The count expected for equilibrium distribution of active malonate is 1187 × 11/25 = 522: that observed was 722. So considerable exchange was observed. The high observed activity of the barium malonate samples was attributed to decomposition of the complex salt by barium ions (barium ions caused visible precipitation from solutions of the complex salt within 0·5 hr., but the exchange solution had to be kept to ensure precipitation of sufficient barium malonate).

Potassium Ferricyanide.—"AnalaR" potassium ferricyanide was used. Susceptibility determinations (units as before are tabulated).

Temp. (K)	χ_g.	χ_M.	χ_M. (corr.)	$10^4/\chi_{M.\ corr.}$
297·48°	6·95 (cf. I.C.T.)	2287	2414·8	4·150
198·0	9·95 ± 0·02	3275	3402·8	2·939
98·1	18·20 ± 0·01	5990	6117·8	1·634

A plot of $1/\chi_{M.\ corr.}$ against T gave a straight line with an intercept on the temperature axis at −43° K. So the magnetic moment is 2·50 B.M. These results differ from those of Ishiwara (*Sc. Rep. Tôhoku Univ.*, 1914, **3**, 303) and Welo (*Phil. Mag.*, 1928, **6**, 481), who obtained a non-linear relation.

Exchange experiments. An aqueous solution was prepared containing 0·282 mole/l. of potassium [^{14}C]cyanide and 0·113 mole/l. of potassium ferricyanide. Separation was achieved by two procedures: (i) addition of ethyl alcohol to precipitate potassium ferricyanide and (ii) addition of cadmium nitrate to precipitate cadmium ferricyanide. "Free" cyanide was precipitated in both cases by addition of silver nitrate. The activities of different samples of silver cyanide differed slightly owing to the friable nature of the precipitate which curled on being dried, but all activities were within 3% of 2000 counts/min., including those for samples which had not been mixed with ferricyanide. The low activity observed in the ferricyanide samples remained constant, though the mixed solutions were kept for periods varying from a few seconds to 64 hr. The activity observed for the potassium ferricyanide sample was 17 counts/min., attributed to the presence of ^{40}K. The activity observed in the case of the cadmium ferricyanide samples range from 14 to about 21 counts/min. The precipitate was very fine (almost gelatinous) and difficult to wash, and the observed activity was attributed to contamination by "free" cyanide. The experiment was conducted at the normal pH (9·5). At higher acidities a very slow apparent exchange was observed but the gradual appearance of a blue colour indicated side reactions. These results are in agreement with those of Adamson, Welker, and Volpe (*J. Amer. Chem. Soc.*, 1950, **72**, 4030).

The foregoing experiments showed that potassium ferrioxalate and ferrimalonate had moments corresponding to 5 unpaired spins and that both showed exchange with labelled ligand groups; also that potassium ferricyanide had a moment corresponding to one unpaired spin and showed negligible exchange.

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