The subsequent filtration completely removed the finely divided $Cr(OH)_3$ which was formed during the course of the reaction. The clear red filtrate was cooled to 0° and neutralized carefully with concentrated hydrochloric acid; the temperature of the mixture was not allowed to rise above 25°. When the solution had been only partially neutralized, a considerable amount of ethylenediamine hydrochloride precipitated. and was removed by filtration after the solution had been neutralized. This filtrate was placed in a vacuum desiccator over phosphorus pentoxide; the solution was left there for twelve hours and the precipitate formed was removed by filtration. This procedure was repeated twice more; in all three cases the material was colorless ethylenediamine hydrochloride. The next two 12-hour evaporations yielded impure $[Cr(en)_3]Cl_3$. This product was purified according to Pfeiffer's[6] method. The yields were never over 25% of the theoretical.

Triethylenediamine chromium(III) chloride, at least in worthwhile yields, does not result from a similar treatment of ordinary hydrated chromic chloride. which contains dichlorotetraquo chromic chloride and chloropentaquo chromic chloride.

A question as to validity of the simple hydrate isomerism as shown by the formulas

$$[Cr(H_2O)_4Cl_2]Cl\cdot 2H_2O \rightleftarrows [Cr(H_2O)_5Cl]Cl_2\cdot H_2O \rightleftarrows [Cr(H_2O)_6]Cl_3$$

seems to arise. To produce $[Cr(H_2O)_6]Cl_3$ it is necessary to have a very high concentration of HCl (a saturated solution at 0°).[4] In the substitution of ethylenediamine for water and for chloride ion the chloride ions are normally more readily replaced. In dilute solutions of $[Cr\ en_2Cl_2]Cl$ and of $[Cr\ en_3]Cl_3$ the final product on standing is $[Cr\ en_2(H_4O_2)_2]Cl_3$. The dichloro compound reacts with water more rapidly than the triethylenediamine.

It does not seem logical that a compound of the formula $[Cr(H_2O)_4Cl_2]Cl$ should result in a different product with anhydrous ethylenediamine than one of the formula $[Cr(H_2O)_6]Cl_3$. The explanation of this more or less classical example of hydrate isomerism proposed by Werner and others[7] is undoubtedly more complicated than was supposed. The molecular conductivity and the molecular weight determinations on the tetrahydrate are in agreement with the simplest formula but the chemical properties seem difficult to explain on the basis of the simplest formula.

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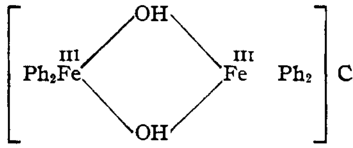
[6] Pfeiffer. *Z. anorg. Chem.*, **29**, 113 (1901).

[7] See Thomas. "Complex Salts." D. Van Nostrand Co., Inc., New York. N. Y., 1924. pp. 28 ff., and Schwarz (translation by Bass) "The Chemistry of the Inorganic Complex Compounds." John Wiley and Sons, Inc., New York. N. Y., 1923. pp. 45 ff.

The Magnetic Susceptibility of the Brown Ferric Phenanthroline Complex

BY L. MICHAELIS AND S. GRANICK

During the study of the magnetic properties of some complex iron compounds of biological interest the problem arose as to how much the mutual interaction of closely packed iron atoms in a polynuclear complex may influence the susceptibility. It seems unavoidable to postulate an iron–iron bond for $Fe_2(CO)_9$[1,2] but, beside this rather exceptional case, no iron complex has been known in which the value of the susceptibility would compel the assumption of Fe–Fe interaction of any appreciable magnitude, except for one case published by Gaines, Hammett and Walden.[3] These authors have described a brown well-crystallizable complex of ferric iron with *o*-phenanthroline which they proved to be binuclear with the following structure (Ph = Phenanthroline)



They have reported a susceptibility of this complex corresponding to an effective magnetic dipole moment of as little as 1.4 Bohr magnetons per gram atom of iron. Since the moment of any ferric complex in which there is no appreciable Fe–Fe interaction can according to theory never be smaller than 1.73 BM even upon the assumption of complete absence of orbital contributions, the authors have suggested an Fe–Fe interaction due to the closeness of the two iron atoms within the binuclear complex. In view of the importance of this case for more general conclusions, we undertook to repeat this measurement. The complex can be easily prepared according to those authors. It forms brown crystals which, when thoroughly dried, having no water of crystallization, should contain 11.1% iron. All of our various samples, prepared independently, showed exactly 11.1% iron, as an average of many well-agreeing analyses. We recommend especially for this analysis the precipitation of iron hydroxide from the complex with alkali, collecting it on an asbestos mat filter, washing with a dilute salt

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[1] H. M. Powell and R. V. S. Ewens. *J. Chem. Soc.*, 286 (1939).

[2] Linus Pauling. "The Nature of the Chemical Bond." Cornell University Press. Ithaca. N. Y., 1939. p. 238.

[3] A. Gaines. L. P. Hammett and G. H. Walden. THIS JOURNAL, **58**, 1668 (1936).

solution (to avoid peptization), with a small portion of alcohol, and again with salt solution, dissolving in sulfuric acid, reducing with hydrogen sulfide and titrating with permanganate.

Magnetic measurements were performed both with the solid, finely powdered, and with aqueous solutions. The method was the one recently described,[4] a modified Gouy method using the double vessel of Freed and Kasper, and reading the lines of deflection on a microscopic scale at the pointer of a damped semi-micro balance. Calibration for the particular vessel used, with the pole distance used (1.39 cm.), showed that for 10 amperes one line of deflection corresponds to an increment of susceptibility = 4.37×10^{-10} cgs. The actual measurements were performed with lower current intensities so as to bring about conveniently measurable deflections. They are recalculated for 10 amperes. This recalculation is based on the agreeable property of the magnet used, that for pole gaps not smaller than 1 cm. the deflection is strictly proportional to the square of the amperage. at least up to 10 amperes.

One experiment will be described in detail. A solution (almost saturated) containing 3.063% of the substance, was filled into the upper compartment of the double vessel, the lower compartment being permanently filled with a 1% agar gel. The deflection measured at 6.90 amperes and recalculated to 10 amperes, was +185 lines. Water gave, under equal conditions, −87 lines. The difference, +272, corresponds to an increment of volume susceptibility, due to the solute, of $+1.19 \times 10^{-6}$ c. g. s. The correction for the difference of the diamagnetic contribution of the solute (according to Pascal) and of the water displaced by it is too small to be worthy of consideration. The result is: the susceptibility per gram-atom of Fe, $10^6\chi_{Fe} = 1970$, at 24°, and the effective moment, calculated according to the simple Curie law, is found to be 2.10 BM.

The same method, for potassium ferricyanide, in many experiments with the solid and with solutions down to $^1/_{300}$ molar at slightly varied room temperatures, gave values for μ_{eff} all in the range from 2.33 to 2.40, in agreement with acknowledged values. Table I shows the result of several experiments carried out with samples of the substance prepared independently.

For the solid, the values given in Table II were obtained.

TABLE I

MEASUREMENT OF SOLUTIONS

Preparation	Concn., %	Temp., °C.	Susceptibility per gram atom of Fe, $\chi_{Fe} \times 10^6$	Effective moment, μ_{eff}
1	3.063	24	1970	2.17
2	2.900	24	1995	2.18
3	2.961	23	1810	2.08

TABLE II

MEASUREMENT OF THE SOLID COMPOUND

Preparation	Temp., °C.	$10^6 \times \chi_{Fe}$ Uncorrected	$10^6 \times \chi_{Fe}$ Corrected for diamagnetism	$\mu_{eff.}$
1	24	2100	2380	2.38
2	24	2200	2480	2.42
3	23	2230	2510	2.44

A slightly higher value is obtained for the solid than for the dissolved state. This difference appears to be greater than the limits of error.

At any rate, no values in the neighborhood of those reported by the authors quoted were obtained. Our values do not suggest any Fe–Fe interaction of appreciable magnitude but lend themselves to the same interpretation as for ferricyanide ion, which, according to Pauling, may be conceived as an octahedral complex with six covalent d^2sp^3 bonds, allowing for the magnetic effect of one unpaired electron slightly increased by incompletely quenched orbital contributions. In the phenanthroline complex, two octahedra share an edge, of which the two corners are represented by oxygen atoms. In $Fe_2(CO)_9$, two octahedra share a face, so that the distance of the two central Fe atoms is smaller than in the case of a shared edge. Perhaps this is the reason why Fe–Fe interaction is strong in the carbonyl compound, but not obvious in the phenanthroline complex.

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The Synthesis of Aldehydes from Acylhydrazides

BY CARL NIEMANN AND JOHN T. HAYS[1]

The reaction

$$RCONHNHSO_2Ar + OH^- \longrightarrow RCHO + ArSO_2^- + N_2 + H_2O$$

which has been used for the preparation of a number of substituted benzaldehydes[2] and hetero-

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[4] L. Michaelis, THIS JOURNAL, **63**, 2446 (1941).

[1] Present address, Hercules Experiment Station, Wilmington, Delaware.

[2] (a) McFadyen and Stevens, *J. Chem. Soc.*, 584 (1936); (b) Hill and Short, *ibid.*, 260 (1937); (c) Harington and Pitt-Rivers, *ibid.*, 1101 (1940); (d) Natelson and Gottfried, THIS JOURNAL, **63**, 487 (1941); (e) Ungnade, *ibid.*, **63**, 2091 (1941); (f) Niemann, Benson and Mead, *ibid.*, **63**, 2204 (1941).