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Citation: The Journal of Chemical Physics **6**, 462 (1938); doi: 10.1063/1.1750292 View online: http://dx.doi.org/10.1063/1.1750292 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/6/8?ver=pdfcov Published by the AIP Publishing

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A Determination of the Magnetic Susceptibilities of Certain Inorganic Complex Compounds

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A standard method used in the determination of the gyromagnetic effect has been so modified as to permit the determination of magnetic susceptibilities. Its use is suggested for the determination of the susceptibilities of complex compounds, since it utilizes weak fields, and also requires only a small amount (less than 0.5 g) of the material to be tested. The susceptibilities of some compounds containing NO have been measured.

WORK done by Pauling¹ and others has given an impetus to the determination of magnetic susceptibilities by showing that a knowledge of the susceptibility of a compound limits the number of structures which that compound may possess; in some instances a unique determination of structure is possible.

Since a great many of the complex compounds of the transition elements, to which these ideas are primarily applicable, can be prepared in only small quantities, we sought a method by which susceptibilities might be determined using only small quantities of material. Initially the use of weak fields was fortuitous. Subsequently we found that a number of compounds exist whose susceptibilities change from large and negative in the presence of weak fields to positive in the presence of intense fields. Further work is being done on susceptibilities in weak fields.

EXPERIMENTAL

The method here employed for determining magnetic susceptibilities consists in maintaining a suspended specimen in torsional vibration by the periodic imposition of a magnetic field of suitably adjusted intensity. A similar arrangement has been used in investigating the gyromagnetic effect, and was introduced by Einstein and de Haas in 1915. It has subsequently been developed by other workers, as for example Coeterier.²

The substance whose susceptibility is to be measured is suspended from a quartz fiber between the poles of an electromagnet. The speci-

men, which is in the shape of a cylinder whose length is large compared to its diameter, will experience a torque such as will tend to align it parallel to the field if it is paramagnetic, or perpendicular to the field if it is diamagnetic. The deflecting torque will be equal to the product of four terms: (1) the square of the field; (2) the susceptibility of the specimen; (3) a function of the angle between the axis of the specimen and the direction of the magnetic field; and (4) a function of the size and shape of the specimen. The measurement of the deflecting torque permits the calculation of (2) provided (1), (3)and (4) are known. However, (3) and (4) would be difficult to calculate for any container of an easily fabricated shape. On the other hand, (3)and (4) remain constant as long as the size and shape of the container, and the angle of deflection, remain constant. If one restricts oneself to the determination of relative susceptibilities, therefore, these quantities need not be known. This restriction at the same time obviates the necessity of calculating the absolute values of the deflecting torque, and of (1), the magnetic field. These may be taken as proportional to the angle of deflection, and the current in the electromagnet respectively.

Instead of determining the deflecting torque directly, the following procedure was used. The specimen was so set that in its equilibrium position, without the application of any field, its axis was at forty-five degrees to the direction of the magnetic field. The magnetic field was then impressed periodically in such a way as to build up oscillations. A mechanism to be described later ensured that the magnet would always be turned on and off at precisely the same angles.

¹ Pauling, J. Am. Chem. Soc. 53, 1367, 3225 (1931).

² Coeterier and Scherer, Helv. Phys. Acta 5, 217 (1932).

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R	70.0	80.0	100.0	120.0	150.0	200.0	300.0	400.0
0	39.90	35.05	28.05	23.40	18.70	14.05	9.30	7.00
RO	2793	2804	2805	2808	2805	2810	2790	2800

TABLE I.

With a given current passing through the magnet, the oscillations would build up until the energy per cycle supplied by the magnet,

 $\int_{\theta_1}^{\theta_1} Ld\theta$, was equal to the energy dissipated per

cycle by air damping. From then on, the specimen would oscillate with constant amplitude. Any change in the current through the magnet would change the magnetic field, and thereby change the energy input per cycle, and consequently the amplitude.

A comparison of the susceptibilities of two substances was effected by placing successively samples of each in the capsule and adjusting the resistance in the magnet circuit until the amplitudes were the same in each case. Since the magnetic field was applied over the same angles to a container of the same size and shape, the only variables were the susceptibilities, the masses, and the magnetic fields. Therefore:

$$m_1\chi_1 + m_0\chi_0 = k'/H_1^2 = CR_1^2,$$

 $m_2\chi_2 + m_0\chi_0 = k'/H_2^2 = CR_2^2,$

where, since H is proportional to 1/R, the reciprocal of the total resistance in the magnet circuit, this more convenient quantity is used. $m_{0\chi_0}$ is the product of mass and susceptibility for the empty capsule. Its value was determined by a separate experiment in which the empty capsule was oscillated with the same amplitude as was attained by the capsule containing the specimens. This gives the additional equation,

$$m_0\chi_0 = k'/H_0^2 = CR_0^2,$$

which permits the elimination of $m_0\chi_0$ from the preceding equations giving

$$m_1\chi_1 = C(R_1^2 \pm R_0^2),$$

$$m_2\chi_2 = C(R_2^2 \pm R_0^2),$$

$$\frac{m_1\chi_1}{m_2\chi_2} = \frac{(R_1^2 \pm R_0^2)}{(R_2^2 \pm R_0^2)},$$

where the plus sign is to be taken if the susceptibilities of the capsule and the contained specimen are of opposite sign, otherwise the minus sign.

The assumption that the magnetic field is proportional to the reciprocal of the total resistance in the circuit requires verification. For this purpose the magnetic field, as measured by a ballistic galvanometer and coil, was plotted against the total resistance in the circuit. A typical set of data is reproduced in Table I.

The maximum deviation from the mean is about $\frac{1}{2}$ percent, which indicates an accuracy sufficient for our purpose.

The magnet is of the conventional type, with a core of silicon steel. It is wound with 5100 turns of No. 20 copper wire, and when excited by a 40-volt d.c. generator with 250 ohms in series, gives a field of approximately 300 oersted. The generator is driven by a $\frac{1}{2}$ horsepower synchronous motor. In operation the magnet is connected to the generator through a set of variable resistances, a commutator, and a relay. The commutator is turned by a spring when an escapement mechanism is released on closing the relay; the commutator's alternately insulating and conducting segments permit current to pass only every other time that the relay is closed. The electrical circuit contains in addition two switches, by the proper operation of which the resistances in the circuit may be measured on a Wheatstone bridge.

The relay is closed when a spot of light reflected from a mirror mounted on the moving suspension falls on a photo-cell (Fig. 1). The activation of the photo-cell increases the grid potential of the thyratron sufficiently to permit the passage of the current which closes the relay. This mechanism ensures the synchronization of the periodic magnetic field with the torsional vibrations of the suspended capsule.

The suspension is a quartz fiber (Fig. 2). To this is attached a Pyrex glass rod on which are mounted two mirrors, one for visual observation of the amplitude of oscillation, and the other for reflecting the spot of light which actuates the

		m	R	R_0	C
Mohr's salt	31.5	0.5298	441.5	69.17	0.836×10-10
Petric alum Potassium ferricyanide	29.4 6.94	.4655	398.9		.834 × 10 ⁻¹⁰

TABLE II.

photo-cell. At the bottom of this rod is the cradle which carries the cylindrical specimen.

The apparatus was calibrated in the following way. Using the equation $m\chi = C(R^2 \pm R_0^2)$, the constant *C* was determined by using three different salts—Mohr's salt, ferric alum, and potassium ferricyanide. The values obtained are shown in Table II.

All measurements were made at 27°C, using the susceptibilities as given in the *International Critical Tables* after correcting to 27°. The excellent agreement is certainly accidental, since weak fields (<300 oersted) were used. We consider our results reliable to 2 percent.

PREPARATION AND ANALYSIS OF COMPOUNDS

When dry NO is passed into a solution of metallic sodium in liquid ammonia, the original intense blue of the solution is rapidly bleached, and subsequent evaporation of the ammonia leaves a cake of very finely crystalline, colorless material. This material rapidly decomposes in water, giving off nitrous oxide, and leaving sodium hydroxide in solution. For this compound Zintl and Harder³ have suggested the formula NaNO. Its reactions are entirely distinct from those of sodium hyponitrite, which has the same empirical formula. Molecular weight determinations have not been made, since it decomposes in all solvents so far tried.

The ferrous ammonium sulphate, ferric ammonium sulphate, and potassium ferricyanide were prepared and purified by standard methods, and these products were used in calibrating the apparatus.

The sodium nitroso-pentanitro-cobaltiate dihydrate, $Na_3[Co(NO)(NO_2)_5] \cdot 2H_2O$, was prepared by passing dried and purified nitric oxide into a flask containing a solution of one mole of cobaltous chloride, to which five moles of sodium nitrite were added at intervals, with constant

³ Zintl and Harder, Ber. 66B, 760 (1935).

stirring, and the whole kept at 0°C. The crystals, which formed after standing, were filtered off.

A similar method was used with the nitrosopentammine cobalt dichloride, $[Co(NO)(NH_3)_5 Cl_2 \cdot 5H_2O]$, the chief difference being that the solid cobaltous chloride was placed in the reaction flask, and five moles of ammonium hydroxide were added at intervals at room temperature. The product was then filtered off.



FIG. 1. Diagram of apparatus.

FIG. 2. Cradle and carriage.

In both preparations, care was taken to exclude air from the reaction flask.

The analysis of the first complex involves some unusual reactions, but appears to be accurate. Concentrated sulphuric acid was added to the complex in a stream of carbon dioxide, and the evolved nitric oxide reduced over hot copper. The nitrogen formed was collected and measured in a gas burette containing a strong potassium hydroxide solution. The copper oxide formed was reduced with hydrogen and the evolved water collected in a P_2O_5 tube. Sulphur dioxide was bubbled through the sulphuric acid residue, and a little water added to ensure complete hydrolysis. The evolved nitric oxide was treated as before. The equations for the analysis are:

 $2Na_{3}[Co(NO)(NO_{2})_{5}]2H_{2}O+5H_{2}SO_{4}\rightarrow$ $2NO+4H_{2}O+2CoSO_{4}+10HNO_{2}+3Na_{2}SO_{4}$ $10HNO_{2}+10HOSO_{2}OH\rightarrow$ $10HOSO_{2}ONO+10H_{2}O$

$$10\text{HOSO}_2\text{ONO} + 10\text{H}_2\text{O} + 5\text{SO}_2 \rightarrow \\ 10\text{NO} + 15\text{H}_2\text{SO}_4$$

$Na_3[Co(NO)(NO_2)_5] \cdot 2H_2O$	THEORY	Experimental
Weight of N ₂ from NO	0.00165	0.0016
Weight of N ₂ from NO ₂	.00827	.0082
Weight of water of crystallization	.0503	.0502

TABLE III.

TABLE IV.

$[Co(NO)(NH_3)_5]Cl_2 \cdot 5H_2O$	THEORETICAL	Experimental
Weight of N2 from NO	0.0272	0.0268
Weight of NH4Cl formed	.2077	.2024
Weight of water of crystallization	.1398	.1396

The results of the analysis are tabulated in Table III.

The analysis of the second complex was made by heating the compound mildly in a stream of carbon dioxide, collecting the ammonium chloride and water formed, and reducing the evolved nitric oxide to nitrogen as before. The ammonia evolved was absorbed by bubbling the gases through concentrated sulphuric acid The equations for the analysis are:

$$\begin{bmatrix} Co(NO)(NH_3)_5 \end{bmatrix} Cl_2 \cdot 5H_2O \rightarrow \\ NO+2NH_4Cl+3H_2O+3NH_3+Co(OH)_2 \end{bmatrix}$$

 $Co(OH)_2 + CO_2 \rightarrow CoCO_3 + H_2O.$

The results of the analysis are tabulated in Table IV.

As an additional identification, the nitrosopentammine complex was refluxed with dilute and concentrated hydrochloric acid, to form the pink aquo-pentammine and the red violet chloropentammine complexes, respectively.

Results of Magnetic Susceptibility Measurements

Of the three compounds whose susceptibilities were measured, only one, $[CoNO(NH_3)_5Cl_2]$. $5H_2O$, was paramagnetic in weak fields. The data for this compound are given below.

т	R	R_0	С
0.2839	271.7	69.17	0.834×10^{-10}

Substituting these values we obtain 23.1×10^{-6} . This value for the susceptibility indicates between two and four unpaired electrons, in apparent contradiction to the value quoted by Pauling, which indicates almost exactly two. Possible explanations of this discrepancy might be (1) the weak fields with which our measurements were made, or (2) the different number of molecules of water of hydration which our compound contained.

NaNO is diamagnetic at all field strengths attainable with our apparatus.

The compound K_3 [CoNO(NO₂)₅] is apparently a transition between the two previous cases. It is diamagnetic in weak fields, becoming gradually paramagnetic as the field strength is increased. This unexpected variation of susceptibility with field strength requires a modification of apparatus which is now being made.

We would like to suggest tentatively the following explanation for the susceptibilities of these three compounds. When NO enters into combination with a sufficiently electropositive atom or radical, the NO is actually reduced to a NO⁻ ion with the structure :N :: O:. This occurs with the compound NaNO. When the combining radical, as in Co(NH₃)₅, is less electropositive the electron structure is that suggested by Pauling, in which the NO group contains two three electron bonds. Finally, the NO in the compound K₃[CoNO(NO₂)₅] represents transition between these two extremes.