[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Magnetic Moments of Rhodium(III) Salts

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The molar magnetic susceptibilities of $RhCl_3$, $Rh_2(SO_4)_3 \cdot 6H_2O$, and $Rh_2(SO_4)_3 \cdot 14H_2O$ were determined by the Gouy method to be $(-7.5 \pm 2.1) \times 10^{-6}$, $(-104 \pm 5) \times 10^{-6}$ and $(-149 \pm 21) \times 10^{-6}$ respectively. The low moments cannot be accounted for by exchange demagnetization but must be due to complex formation. The "residual paramagnetism" of $+85 \times 10^{-6}$, $+66 \times 10^{-6}$ and $+95 \times 10^{-6}$ is attributed to low-lying excited states.

The development of magnetic susceptibility theory has been slowed by the scarcity of data for the heavier transition elements. The few data that are available indicate that the "orbital quenching-spin only" treatment so successful for compounds of the first transition period does not work for succeeding periods. Instead, the magnetic moments are invariably lower than the "spin-only" prediction. In complex compounds, low moments may be explained by electron pairing brought about by inner-orbital complex formation. In simple compounds, low moments may also be explained by exchange demagnetization provided that the concentration of magnetic carriers is high enough.[1] We have in this work investigated some rhodium compounds in an attempt to decide between the two possibilities. If the observed low moment is due to exchange demagnetization, dilution of the magnetic carrier should increase the magnetic moment per rhodium atom.

Three compounds, $RhCl_3$, $Rh_2(SO_4)_3 \cdot 6H_2O$ and $Rh_2(SO_4)_3 \cdot 14H_2O$ were prepared in high purity and their magnetic moments determined by the Gouy method. The trichloride represents magnetically concentrated material in which the distance between rhodium atoms is smallest and exchange, perhaps coupled through the halogen, is most favored. In the hydrated sulfates, rhodium atoms are farther apart and exchange is less favorable.

Experimental

Preparation of Compounds.—Rhodium metal was obtained from the American Platinum Works as a fine powder stated to assay at least 99.5% Rh. Spectroscopic analysis indicated In, Pb and Ca of about 0.05% each. Rhodium trichloride was prepared by successively heating Rh powder in a stream of dry electrolytic chlorine for five days at 800°, reducing with hydrogen for one-half hour at 400°, and rechlorinating for three days at 800°. Unless the rhodium is extremely finely divided, complete conversion to $RhCl_3$ is not obtained. Analysis was performed after Wöhler and Müller[2] for both rhodium and chlorine. Chlorine was determined by reducing $RhCl_3$ with hydrogen and analyzing the emergent HCl gravimetrically for chlorine. The residual metal, after cooling in CO_2 to avoid hydrogen absorption, was weighed as pure rhodium. The product $RhCl_3$ analyzed 49.38% Rh and 50.60% Cl compared to 49.16% Rh and 50.84% Cl theoretical.

Yellow rhodium sulfate, $Rh_2(SO_4)_3 \cdot 14H_2O$, was made by dissolving freshly precipitated rhodium trihydroxide in cold dilute sulfuric acid and crystallizing by evaporation under vacuum at 0°. Rhodium was determined by electrodeposition from acidic solution as described by Krauss and Umbach.[3] Sulfate was determined as barium sulfate after removal of rhodium. Water of hydration was determined by standard micro-combustion methods for hydrogen. Results of the analysis gave 27.64% Rh, 38.29% SO_4 and 34.4% H_2O. The theoretical values for $Rh_2(SO_4)_3 \cdot 14H_2O$ are 27.58, 38.62 and 33.80, respectively.

Red rhodium sulfate, $Rh_2(SO_4)_3 \cdot 6H_2O$, was prepared by dissolving the yellow form in water and evaporating to dryness at 100° as described by Krauss and Umbach. The product analyzed 34.2% Rh, 47.7%SO_4, and 18.4% H_2O compared to 34.18% Rh, 47.86% SO_4, and 17.95% H_2O theoretical for $Rh_2(SO_4)_3 \cdot 6H_2O$. Krauss and Umbach reported this red sulfate to be $Rh_2(SO_4)_3 \cdot 4H_2O$.

Magnetic Measurements.—Magnetic susceptibilities were determined by the Gouy method using the apparatus and procedure described by Kernahan and Sienko.[4] As a check determination the molar susceptibility of sodium chloride was found to be $(-30.1 \pm 1.5) \times 10^{-6}$ compared to the best literature value[5] of -30.2×10^{-6}.

Results

The observed magnetic susceptibilities given in Table I are the results of 15 determinations of each of three samples of each compound. The susceptibilities were field independent. The low moment of $RhCl_3$ is in substantial agreement with the value -17×10^{-6} previously reported by Cabrera and Duperier.[6] The moments of the sulfates have not been previously determined. Assuming that the susceptibilities are additive and using the diamagnetic increments given in Table II the susceptibility contribution of Rh^{+3} is $+65 \pm 8 \times 10^{-6}$, $+44 \pm 12 \times 10^{-6}$ and $+73 \pm 20 \times 10^{-6}$ in $RhCl_3$, $Rh_2(SO_4)_3 \cdot 6H_2O$ and $Rh_2(SO_4)_3 \cdot 14H_2O$, respectively. Thus, the magnetic moment of rhodium atoms is essentially zero, and dilution makes no significant difference in its value.

TABLE I

EXPERIMENTAL MAGNETIC SUSCEPTIBILITIES AT 25°

Compound	Molar susceptibility	Probable error
$RhCl_3$	-7.5×10^{-6}	$\pm 2.1 \times 10^{-6}$
$Rh_2(SO_4)_3 \cdot 6H_2O$	-104×10^{-6}	$\pm 5 \times 10^{-6}$
$Rh_2(SO_4)_3 \cdot 14H_2O$	-149×10^{-6}	$\pm 21 \times 10^{-6}$

TABLE II

MOLAR DIAMAGNETIC CORRECTIONS

Group	$\chi \times 10^6$	Source
$SO_4^=$	-38 ± 6	Hoare and Brindley[7]
Cl^-	-24.2 ± 2.0	Hoare and Brindley[7]
H_2O	-13.0 ± 0.1	Auer[8]

Discussion

Exchange interaction between two magnetic atoms rapidly decreases with increasing separation

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(1) J. H. VanVleck, "Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932, p. 314.

(2) L. Wöhler and W. Müller, *Z. anorg. allgem. Chem.*, **149**, 125 (1925).

(3) F. Krauss and H. Umbach, *ibid.*, **180**, 42 (1929).

(4) J. Kernahan and M. J. Sienko, THIS JOURNAL, **77**, 1978 (1955).

(5) W. Klemm, *Z. anorg. allgem. Chem.*, **244**, 392 (1940).

(5) B. Cabrera and A. Duperier, *Proc. Phys. Soc.*, **51**, 1845 (1939).

(7) F. E. Hoare and G. W. Brindley, *ibid.*, **49**, 623 (1937).

(8) H. Auer, *Ann. Physik.*, **18**, 593 (1933).

between the atoms. Thus, if an atom has an appreciable moment that is quenched by exchange demagnetization with a neighbor, then increasing the distance between neighbors should restore the full moment. Since there is apparently no such effect observed in the highly hydrated sulfates, the low moment of rhodium in these compounds should not be attributed to interactions between neighboring Rh atoms. Rather, the low moment must be due to complexing.

The Rh^{+3} ion is probably of a d^6 configuration corresponding to 6.70 Bohr magnetons for the unperturbed ion or 4.90 for spin-only. In $RhCl_3$, the observed moment is essentially zero and suggests an inner orbital $d^2\ sp^3$ complex. It is probable that Rh is coördinated octahedrally to six chlorine atoms in some sort of infinite three-dimensional complex similar to $CrCl_3$. In atomic orbital language, electrons from the six chlorine atoms occupy two of the 4d, one 5s, and three 5p orbitals of the rhodium forcing the six electrons of Rh to pair up in the remaining three 4d orbitals. Alternatively, by the crystalline field method of Penney and Schlapp,[9] the cubic field of the surrounding chlorine octahedron could split the ^5D level so that the triply degenerate $d\epsilon$ level is lower and accommodates the six electrons as pairs. Finally, by the molecular orbital method, the low moment could be explained if the three $d\epsilon$ non-bonding orbitals were lower in energy than the two $d\gamma_2$ antibonding orbitals.

Conductometric and spectroscopic investigation of the aqueous solutions of the sulfates, to be reported in a following paper, suggest that in yellow $Rh_2(SO_4)_3 \cdot 14H_2O$, Rh is present as the complex $Rh(H_2O)_6^{+++}$ and in red $Rh_2(SO_4)_3 \cdot 6H_2O$ as a sulfato complex. In either case, the observed low moment can be accounted for as in $RhCl_3$, assuming sixfold coördination of oxygen atoms to the rhodium.

According to Klemm,[10] Rh^{+3} has a diamagnetic increment of -22×10^{-6}. This means that there is a "residual paramagnetism" of $+85 \times 10^{-6}$, $+66 \times 10^{-6}$ and $+95 \times 10^{-6}$ for the complexes in $RhCl_3$, $Rh_2(SO_4)_3 \cdot 6H_2O$ and $Rh_2(SO_4)_3 \cdot 14H_2O$, respectively. Such "residual paramagnetism" could be due to the existence of low-lying excited electronic energy levels such as apparently exist in Co(III) complexes.[4] Since rhodium, like cobalt, consists 100% of a single isotope, Rh^{103} with nuclear spin 1/2, it should be relatively easy to detect these low-lying states by investigating the nuclear resonance shift as a function of temperature.

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[9] W. G. Penney and R. Schlapp, *Phys. Rev.*, **42**, 666 (1932).

[10] W. Klemm, *Z. anorg. allgem. Chem.*, **246**, 361 (1941).

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The Crystal Structure of an Ethylene–Palladium Chloride Complex

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The crystal structure of ethylene–palladium chloride has been determined from single crystal Weissenberg data. The orthorhombic cell dimensions are $a = 15.41$ Å., $b = 9.29$ Å., $c = 7.23$ Å. The complex is a dimer, $(PdCl_2C_2H_4)_2$, with four dimers per unit cell. The coördination about the palladium atoms is planar square, the palladium atoms are joined by a bridge of two chlorine atoms, the ethylene groups are attached to the palladium atoms in the *trans* position. Electron density maps indicate that the axis of the ethylene molecule is perpendicular to the plane of the dimer and that the center of the ethylenic double bond lies in the plane of the dimer.

Introduction

Complexes of olefins with platinum and palladium chloride[1–7] and with other metals[8] have been studied previously by chemical and spectroscopic methods. A crystal structure determination has been reported for a related silver perchlorate–benzene complex[9] and a preliminary structure has been reported for Zeise's salt, $K(PtCl_3 \cdot C_2H_4) \cdot H_2O$.[10,11] In Zeise's salt the orientation of ethylene relative to the platinum atom appears to be similar to its orientation relative to platinum (or palladium) suggested by Chatt for the platinum chloride–ethylene dimer. The results of a study of the crystal structure of the palladium chloride–ethylene dimer which are reported below are in agreement with the structure proposed by Chatt.

When the X-rays scattered by carbon atoms make up only a small fraction of the total scattered rays, it is very difficult to fix their positions accurately, especially when their contribution to the scattered rays is about equal to the error in estimating the structure factors. In addition, the positions of the hydrogen atoms are still more difficult to determine, so that the orientation of the ethylene molecule is unknown. In order to determine the orientation of the ethylenic group the structure of a related olefinic complex, the styrene–palladium chloride dimer, has also been determined and is reported in a separate paper.[12]

Experimental

The complex $(PdCl_2C_2H_4)_2$ (I) was prepared by the method of Kharasch and Ashford.[2] The palladium chlo-

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