It should be possible to find the atomic weight of uranium lead from that of a mixture of uranium and thorium lead if the relative proportions of uranium and thorium in the original mineral are known and if these proportions have not changed through alteration of the mineral, through leaching for instance. It is also necessary to know the relative rates of production of lead by uranium and thorium. A probable value for this at present is Th rate/U rate = 0.36. Values computed for certain minerals are given in the following table. The isotopic weight of Pb^{208} is taken as 207.96.

	U, %	Th, %	Average atomic weight	Atomic weight uranium lead	Approximate age, million years
Cyrtolite, Hybla, Ont., Can.	0.529[18]	0.080[18]	206.20	206.10	600
Uraninite, Besner, Ont., Can.	67.6[19]	1.57[19]	206.05	206.04	800
Bröggerite, Moss, Norway	67.2	4.4	206.06[20]	206.02	800
Uraninite, Wilberforce, Can.	53.5	10.4	206.20[21]	206.08	1100
Uraninite, Black Hills, South Dakota, U. S. A.	66.9	2.0	206.07[22]	206.05	1500

It is interesting that the minimum value found in this way is not much higher than that found from thorium-free minerals.

Obviously more data of all sorts are highly desirable.

Summary

1. The atomic weights of certain radiogenic leads have been determined.

Source	Atomic weight
Uraninite, Besner Mine, Parry Sound, Ontario, Canada	206.25
Pitchblende, Great Bear Lake, N. W. T., Canada	206.06
Cyrtolite, Hybla, Ontario, Canada	206.20
Cyrtolite I, Bedford, New York, U. S. A.	205.93
Cyrtolite II, Bedford, New York, U. S. A.	206.07
Galena, Yancey County, North Carolina, U. S. A.	207.21
Curite, Katanga region, Africa	206.03

The value for Great Bear Lake material agrees with that found by Marble. That for Katanga curite lead agrees with that found simultaneously by Hönigschmid.

2. It is pointed out that the atomic weight of uranium lead shows little evidence of varying systematically with the age of the mineral source.

3. It is pointed out that the atomic weight of uranium lead appears to be at least as low as 206.00.

CAMBRIDGE, MASS.

RECEIVED JANUARY 18, 1935

(18) Muench, *Am. J. Sci.*, Series V, **25**, 487 (1933).

(19) Ellsworth, *Am. Mineral.*, **16**, 577 (1931); weighted average.

(20) Hönigschmid and St. Horovitz, *Sitzungsb. Kais. Akad. Wien*, **123**, 1 (1914).

(21) Baxter and Bliss, THIS JOURNAL, **52**, 4851 (1930).

(22) Richards and Hall, *ibid.*, **48**, 704 (1926).

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, UNIVERSITY OF WISCONSIN]

The Diamagnetic Susceptibilities of Palladium Salts

BY R. B. JANES

Ni^{II}, Pd^{II} and Pt^{II} have the same type of electronic configuration in the outermost shell, *i. e.*, eight electrons in a d shell. According to the Hund rule for determining the lowest energy state of a free gaseous ion, all three of these ions are in a $^3F_4$ state when free; that is, they should have a resultant spin quantum number of two and a resultant orbital quantum number of three. If the metallic ion in the salts of these metals behaves as a free gaseous ion, the salts of all three elements should be paramagnetic. For nickel salts, in general, the orbital contribution of the Ni^{II} ion to the paramagnetic susceptibility of the salts is largely destroyed by the electric fields of the surrounding ions in the salt molecule, leaving a paramagnetism due only to the spin of the Ni^{II} ion.[1] In the case of platinum for the salts that have been measured the susceptibilities are diamagnetic.[2] The chemistry of palladium as a rule resembles that of platinum, but in a few ways resembles that of nickel. To see whether the magnetic susceptibility of these compounds correlates with their chemical behavior, measurements of the susceptibilities of Pd^{II} salts have

(1) For a general discussion of this see Van Vleck, "Theory of Electric and Magnetic Susceptibilities," also Schlapp and Penney, *Phys. Rev.*, **42**, 666 (1932).

(2) The measurements of the magnetic susceptibilities of Pt salts are collected in a paper by D. M. Bose, *Z. Physik*, **65**, 677 (1930).

been made to determine whether they correspond to those of Ni^{II} or of Pt^{II}. Measurements of the susceptibilities of salts of Pd^{III} and Pd^{IV} also have been carried out.

In all cases powdered crystals of the different salts investigated were used. The magnetic measurements made use of the Gouy method of weighing a rod of the material with and without a magnetic field acting at right angles to the bottom of the tube. The difference in weight is proportional to the susceptibility. In order to obtain absolute values of the susceptibilities, the glass tubes in which the salts were packed were calibrated with an aqueous solution of $NiCl_2$. Measurements were made at room and at liquid air temperatures.

All of the salts were prepared from palladium sponge containing 0.6% platinum and 0.1% iron as impurities. The sponge was kindly furnished by the International Nickel Company for use in this work. The salts were analyzed gravimetrically for palladium by precipitating it as palladium dimethylglyoxime. Some of the complex salts had to be broken down into simple salts before the precipitation.

The palladium compounds investigated are listed below in groups, such that the explanation for all the salts of one group is the same. The susceptibilities are *all diamagnetic* with no appreciable change with temperature.

(1) Pd^{II} salts with only two other ions in the molecule: $Pd(SCN)_2$, $PdCl_2$, $Pd(NO_3)_2$, $Pd(CN)_2$, PdI_2.

(2) Pd^{II} salts with four other groups in the molecule: $PdCl_2{\cdot}2H_2O$, $PdCl_2{\cdot}2NH_3$, K_2PdCl_4, $K_2Pd(CN)_4$, K_2PdI_4, $K_2Pd(SCN)_4$, $K_2Pd(NO_2)_4$.

(3) Pd^{II} inner complex salts: palladium dimethylglyoxime.

(4) Pd^{II} salts where the freezing point data indicate that a double molecule is formed: $(Pd(NH_3)_2Cl_2)_2$.

(5) Pd^{III} salts where the freezing point data indicate that a double molecule is formed: $(Pd(NH_3)_3Cl_3)_2$.

(6) Pd^{IV} salts with six other groups in the molecule: K_2PdCl_6, $PdCl_4{\cdot}2NH_3$.

Ni^{II} salts of the type of group 1 are all strongly paramagnetic with the exception of $Ni(CN)_2$. Of the Pt^{II} salts of this type, only $PtCl_2$ has been investigated and this has been found to be diamagnetic. It is reasonable to suppose that the other Pt^{II} salts of this type are also diamagnetic. One and probably the best explanation of the diamagnetism of the Pd^{II} and Pt^{II} salts of this type, which will also include the case of $Ni(CN)_2$, is that the Hund rule breaks down. That is, the lowest lying level of the metallic ion in these salts is one of zero resultant spin. Together with the assumption that there is no resultant quantized orbital momentum, which is assumed even for the paramagnetic Ni^{II} salts, this gives a zero resultant magnetic moment or diamagnetism. Why it should break down in these cases the writer cannot say, unless the crystalline fields are stronger than in the case of the paramagnetic nickel salts. Another explanation is that the metallic ions lie close enough together so that the spins of neighboring ions couple to give a resultant spin of zero. It would be expected that this coupling would disappear when the lighter anions in the salts were replaced by heavier ones. No such effect has been found. However, this disappearance of a coupling effect would not be expected if the Pd^{II} ions in the crystal lattice are so arranged that there is no anion between two or more of them. No data are available on the crystal structure of the heavier salts of this type. A dilute solution of $Pd(NO_3)_2$ was also found to be diamagnetic, showing that this coupling tendency, if it exists, persists even in this case. There is no evidence from freezing point determinations for the existence of a double molecule so that the hypothetical coupling spoken of above cannot be great enough to give a double molecule.

Ni^{II} salts of the type of group 2 are paramagnetic except for $Ni(CO)_4$ and $K_2Ni(CN)_4$, which are diamagnetic. The several Pt^{II} salts which have been measured are diamagnetic. The breakdown of the Hund rule could be assumed in the case of these diamagnetic salts also but an alternative explanation is offered by Pauling on the basis of the electron pair bond. He predicts that Ni^{II}, Pd^{II} and Pt^{II} salts would be diamagnetic if the four possible electron pair bonds lie in a plane and extend to the corners of a square. The CN groups or whatever groups share these bonds with the Pd^{II} ion must therefore lie on the corners of a square with the Pd^{II} ion in the center and in the same plane.[3] If this is true, only a few Ni^{II} molecules of the group 2 type tend to take this configuration while all Pd^{II}

---

[3] A discussion of Pauling's work and the chemical and x-ray evidence supporting it are reviewed in the 1933 Annual Report of the Chemical Society.

and Pt^{II} molecules of this type assume it. The salt of group 3 is explained in the same way. It thus resembles nickel dimethylglyoxime, which is also diamagnetic.

The diamagnetism of the salts of group 4 can be best explained by assuming a coupling between the spins of pairs of Pd^{II} ions. This coupling is of such a nature that it gives a zero resultant spin and also gives rise to the formation of a double molecule which can be observed in freezing point determinations. This explanation appears necessary for the salt listed in group 5. Otherwise the salt would be made up of single molecules with the Pd^{II} ion possessing an odd spin and therefore paramagnetism under all conditions.

Salts of the type of group 6 exist only in the case of Pt^{IV} and Pd^{IV}. The susceptibility is diamagnetic for the several Pt^{IV} salts that have been measured and for the two Pd^{IV} salts measured in this work. This can be explained in the same way as the diamagnetism of the salts of the group 2 type, that is, either by the breakdown of the Hund rule or by Pauling's theory of the electron pair bond. Here Pauling predicts that the salts of Pd^{IV} and Pt^{IV} are diamagnetic if the six possible electron pair bonds shared by groups in the molecule with the metallic ion extend to the corners of a regular tetrahedron.

The results show that the magnetic susceptibilities of Pd^{II} salts resemble closely those of Pt^{II}. In a few cases the susceptibilities of Ni^{II} salts resemble those of Pd^{II} and Pt^{II}. Only in the case of the dimethylglyoxime salt does Pd^{II} resemble Ni^{II}, exclusively. The corresponding Pt^{II} salt does not exist. The susceptibilities of Pd^{IV} salts closely resemble those of Pt^{IV}.

The author wishes to thank Professor J. H. Van Vleck for his continued interest in this work.

Summary

Using the Gouy method the magnetic susceptibilities of several typical palladium salts have been measured. In all cases the susceptibilities proved to be diamagnetic. An attempt is made to explain this behavior.

MADISON, WIS. RECEIVED JANUARY 18, 1935

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 457]

The Electron Diffraction Investigation of the Molecular Structures of (1) Chlorine Monoxide, Oxygen Fluoride, Dimethyl Ether and 1,4-Dioxane and of (2) Methyl Chloride, Methylene Chloride and Chloroform, with Some Applications of the Results

BY L. E. SUTTON AND L. O. BROCKWAY

The electron diffraction method of investigating the structure of molecules has been sufficiently well developed that it now represents one of the most direct and practical means of obtaining information on bond distances and angles. The present communication gives the results of such investigations upon chlorine monoxide, oxygen fluoride, dimethyl ether and 1,4-dioxane, and the chlorinated methanes. These were made in order to test further the validity of the rule of additivity of atomic radii proposed by Sidgwick[1] and by Pauling,[2] to study the oxygen bond angle and to test the constancy of the carbon–chlorine bond angle. Some of the substances have been previously examined by other workers (as indicated below) but it seemed desirable to repeat their work.

Preparations

Chlorine Monoxide.—Chlorine monoxide was prepared by the method of Bodenstein and Kistiakowsky,[3] omitting the shaking of the reaction tube. Half of the product obtained was distilled off and rejected, in order to remove chlorine, while the remainder was distilled into a suitable container and used for the experiment. The sample was kept at −70° until just before it was used, when the temperature was raised to −40°. Photographs obtained from two separate preparations indicated that there was no appreciable decomposition of the chlorine monoxide.

Dimethyl Ether.—Dimethyl ether was prepared by the method of Krafft[4] and was stored and purified in solution in concentrated sulfuric acid.[5] From this it was regenerated by the addition of water, was dried and transferred to a suitable container at a pressure of 300 mm.

Oxygen Fluoride.—We are indebted to Professor Yost of this Laboratory for two samples of oxygen fluoride. They contained about four or five mole per cent. of oxygen,

---

[1] N. V. Sidgwick, "Annual Reports of the Chemical Society," 1931; "The Covalent Link in Chemistry," Cornell University Press, 1933.

[2] Linus Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932); Linus Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[3] M. Bodenstein and G. B. Kistiakowsky, *Z. physik. Chem.*, **116**, 372 (1925).

[4] F. Krafft, *Ber.*, **26**, 2833 (1893).

[5] E. Erlenmeyer and A. Kriechbaumer, *ibid.*, **7**, 699 (1874).