

20. *Magnetism and Valency. Part I.*  
*Copper and Silver Compounds.*

By SAMUEL SUGDEN.

IN this series of papers it is intended to make a survey of the magnetic moments of substances which exhibit paramagnetism with special reference to the transition elements. Both simple and

complex salts will be studied in order to elucidate the influence of co-ordination as well as the effect of the principal valency of the ion or atom concerned.

It is already well known that changes in principal valency bring about changes in magnetic moment which can be correlated with atomic structure. In general, atoms or ions which contain completed sub-groups possess zero, or very small, magnetic moments and are diamagnetic, whilst those in which the sub-group is incompletely filled are paramagnetic. It is theoretically possible, however, for an atom with an even number of electrons in an incompletely filled sub-group to be diamagnetic. For atoms of the first transition series (Sc to Cu) the magnetic moment in Bohr units (5593 e.s.u.) should lie between

$$\mu_{\alpha} = \sqrt{4s(s+1)} \text{ and } \mu_{\beta} = \sqrt{4s(s+1) + l(l+1)} \quad (1)$$

(compare Stoner, *Phil. Mag.*, 1929, **8**, 250). Here  $s$  is the total spin moment of the electrons in the sub-group, and  $l$  their "orbital" magnetic moment.

Thus  $\mu_{\alpha}$  deals only with the contribution of the electron spin to the magnetic moment and neglects the "orbital" moment, whilst  $\mu_{\beta}$  takes the latter factor into account. It is a remarkable fact that most of the simple salts of elements of the first transition series give moments which are very close to  $\mu_{\alpha}$ . Stoner (*loc. cit.*) suggests that interaction with neighbouring atoms in the solid state or in solution interferes with the  $l$  component and largely eliminates it.

The influence of co-ordination upon magnetic moment has been studied experimentally by a number of workers, notably by Rosenbohm (*Z. physikal. Chem.*, 1919, **93**, 693), and theoretical discussions have been given by Welo and Baudisch (*Nature*, 1925, **116**, 606) and more recently by Pauling (*J. Amer. Chem. Soc.*, 1931, **53**, 1391). Welo and Baudisch trace a relation between the magnetic moment and the "effective atomic number," assuming that the co-ordinated groups are held by shared pairs of electrons; this relation breaks down in a number of cases and need not be further considered here. Pauling's theory is in terms of wave-mechanics and leads to interesting conclusions concerning types of valency linkage and magnetic moment. It will be considered further in Part II of this series in connexion with measurements on nickel compounds.

The present paper is concerned with the data for copper and silver compounds. In the univalent condition the ions of these elements possess a complete sub-group of 10 electrons (in the  $3_d$  level for copper and the  $4_d$  level for silver); hence they should be diamagnetic

and give  $\mu = 0$ . The bivalent ions will have only 9 electrons in this sub-group and should therefore be paramagnetic. For such a sub-group, Pauli's exclusion principle gives  $s = \frac{1}{2}$  and  $l = 0, 1, \text{ or } 2$ ; hence  $\mu_a = 1.73$ , and  $\mu_\beta = 1.73, 2.24, \text{ or } 3.00$ .

The experimental determination of  $\mu$  involves the measurement of the atomic mass susceptibility,  $\chi_A$ , preferably over a range of temperatures so that the constants  $C$  and  $\theta$  in the Weiss law  $\chi_A(T - \theta) = C$  can be evaluated;  $\mu$  is then given by

$$\mu = 2.83\sqrt{C} = 2.83 \sqrt{\chi_A(T - \theta)} \quad . \quad . \quad (2)$$

For many substances, particularly those in which the magnetic atoms are widely separated,  $\theta$  is found to be very small or zero, and the equations reduce to the simple Curie law

$$\chi_A T = C, \quad \mu = 2.83 \sqrt{\chi_A T} \quad . \quad . \quad (3)$$

so that  $\mu$  can be determined by observations of  $\chi_A$  at one temperature only. This method has been adopted in the present series of papers in order to cover as wide a range of compounds as possible, and the values of  $\mu$  quoted in the tables are calculated from equation (3). Some caution must therefore be observed in discussing these values, as anomalies may be due to the neglect of  $\theta$ . Thus Welo has found (*Phil. Mag.*, 1928, 6, 481) that certain iron complexes give large negative values of  $\theta$ . It is hoped later to investigate anomalous substances, *e.g.*, cupric oxide, over a range of temperatures.

The data for copper compounds are collected in Table I. The columns headed  $\chi$  and  $\chi_M$  give the measured susceptibility per g. and per g.-mol. respectively.  $\delta$  is the correction for the diamagnetism of the atoms or groups attached to the copper atom; it is computed from the constants quoted in Table II, which is compiled partly from "International Critical Tables," VI, 349, and partly from Stoner ("Magnetism and Atomic Structure," Methuen and Co., London, 1926, 122). By subtracting  $\delta$  from  $\chi_M$ , the mass susceptibility for a g.-atom,  $\chi_A$ , is obtained, and from this, by equation (3), the magnetic moment  $\mu$ .

It will be seen that the cuprous compounds, except the oxide, are all diamagnetic in accordance with theory. The small paramagnetism of the oxide has been found in several specimens prepared by reduction of Fehling's solution and may be due to a trace of absorbed cupric salt although the analyses show that the substance examined is essentially cuprous oxide.

The cupric compounds are all paramagnetic and, with the exception of the oxide and the acetate, give values of  $\mu$  close to the theoretical value. This is true not only for the simple salts but also for the co-ordinated complexes. Of the latter, two types

are considered, namely, ionised tetrammines and un-ionised chelated compounds with acetylacetone and its homologues. In all these compounds the magnetic moment is close to the value calculated for the spin component only; the orbital component appears to play little part in simple or complex salts of copper. In solution, simple cupric salts obey Curie's law and give  $\mu = 1.92$  (Stoner, *op. cit.*, p. 130).

TABLE I.  
*Copper Compounds.*

No.	Substance.	Ob-server.	<i>t.</i>	$\chi$ .	$\chi_M$ .	$\delta$ .	$\chi_A$ .	$\mu$ .
1	Cu <sub>2</sub> O	S	21°	+0.10	+ 14	- 4	+ 18	0
2	CuCl	"	18	-0.08	- 8	- 20	+ 12	0
3	CuBr	M	17	-0.25	- 36	- 31	- 5	0
4	CuI	"	17	-0.18	- 34	- 45	+ 11	0
	"	S	19	-0.23	- 44	- 45	+ 1	0
5	CuCNS	"	20	-0.22	- 27	- 30	+ 3	0
6	CuO	M	17	+2.90	230	- 4	+234	0.74
	"	S	17	3.17	252	- 4	+256	0.77
7	CuCl <sub>2</sub>	I	19	9.10	1224	- 40	1264	1.72
	"	F	17	9.31	1252	- 40	1292	1.73
8	CuCl <sub>2</sub> ,2H <sub>2</sub> O	"	17	8.35	1424	- 66	1490	1.86
9	CuCl <sub>2</sub> ,2NH <sub>4</sub> Cl	"	17	5.23	1221	-120	1341	1.76
10	CuCl <sub>2</sub> ,2NH <sub>4</sub> Cl,2H <sub>2</sub> O	"	17	4.95	1334	-146	1480	1.85
11	CuCl <sub>2</sub> ,2KCl	"	17	4.28	1213	-102	1315	1.75
12	CuCl <sub>2</sub> ,2KCl,2H <sub>2</sub> O	"	17	4.30	1375	-128	1503	1.87
13	CuCl <sub>2</sub> ,2NaCl	"	17	6.48	1250	- 64	1314	1.75
14	CuCl <sub>2</sub> ,KCl	"	17	6.03	1261	- 51	1312	1.75
15	CuBr <sub>2</sub>	M	17	6.13	1370	- 62	1432	1.82
16	CuSO <sub>4</sub>	"	17	6.72	1072	- 37	1109	(1.60)
	"	F	17	8.6	1372	- 37	1409	1.81
17	CuSO <sub>4</sub> ,5H <sub>2</sub> O	"	17	5.9	1472	-102	1574	1.91
	"	S	19	6.14	1532	-102	1634	1.95
18	Cu(NO <sub>3</sub> ) <sub>2</sub> ,6H <sub>2</sub> O	E	ca.20	5.50	1625	-114	1739	2.02
19	Cu(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ,H <sub>2</sub> O	"	20	3.27	653	- 73	726	(1.31)
20	[Cu4NH <sub>3</sub> ](NO <sub>3</sub> ) <sub>3</sub>	R	18	5.51	1409	- 92	1501	1.87
21	[Cu4NH <sub>3</sub> ]SO <sub>4</sub> ,H <sub>2</sub> O	"	18	5.71	1403	-106	1509	1.87
22	[Cu en]Cl <sub>2</sub>	"	18	7.24	1409	- 88	1497	1.87
23	[Cu en]Br <sub>2</sub>	"	18	4.97	1409	-110	1519	1.88
24	[Cu en](SCN) <sub>2</sub>	"	18	5.89	1411	-124	1535	1.89
25	[Cu en]SO <sub>4</sub> ,2H <sub>2</sub> O	"	18	5.53	1414	-111	1525	1.89
26	[Cu 2py]Cl <sub>2</sub> *	"	18	4.25	1243	-134	1377	1.79
27	[Cu 2acac]	S	16	5.92	1548	- 97	1645	1.95
28	[Cu 2prac]	"	19	4.91	1422	-122	1544	1.90
29	[Cu 2buac]	"	22	4.12	1309	-144	1453	1.85
30	[Cu 2bzac]	"	22	3.23	1246	-176	1422	1.83

en = ethylenediamine.

py = pyridine.

acac = acetylacetone residue, C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>.

prac = propionylacetone residue, C<sub>6</sub>H<sub>9</sub>O<sub>2</sub>.

buac = butyrylacetone residue, C<sub>7</sub>H<sub>11</sub>O<sub>2</sub>.

bzac = benzoylacetone residue, C<sub>10</sub>H<sub>9</sub>O<sub>2</sub>.

References.—E, Endo, *Sci. Rep. Tōhoku*, III, 1925, 14, 479; F, Feytis, *Compt. rend.*, 1911, 153, 666; 1913, 156, 886; M, Meyer, *Ann. Physik*, 1900, 1, 668; R, Rosenbohm, *Z. physikal. Chem.*, 1919, 93, 693; S, Sugden, this paper.

\* For this substance Rosenbohm gives  $\chi_M = 1413$ , which is not in agreement with the formula and the experimental value of  $\chi$ .

The anomalous value found for the oxide may be due to the assumption of a Curie law for this substance which is by no means "magnetically dilute." If the true moment is 1.73, then the value of  $\theta$  in the Weiss equation (2) is  $-1170^\circ$ . This is large, but similar large values of  $\theta$  (up to  $-700^\circ$ ) have been found for basic iron complexes (Welo, *loc. cit.*).

TABLE II.  
*Diamagnetic Corrections.*

		Ions.	
C	- 6.25		
H	- 3.04	Na <sup>+</sup>	- 4
N	- 5.80	K <sup>+</sup>	- 11
O'	- 4.61	NH <sub>4</sub> <sup>+</sup>	- 20
O''	+ 1.73	Cl <sup>'</sup>	- 20
S	- 15.6	Br <sup>'</sup>	- 31
Benzene structure	- 1.5	I <sup>'</sup>	- 45
Double bond	- 5.7	CNS <sup>'</sup>	- 30
Two or more double bonds	- 11.0		
H <sub>2</sub> O	- 13		
NH <sub>3</sub>	- 14		
		NO <sub>3</sub> <sup>'</sup>	- 18
		ClO <sub>3</sub> <sup>'</sup>	- 26
		ClO <sub>4</sub> <sup>'</sup>	- 31
		C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>'</sup>	- 30
		SO <sub>4</sub> <sup>''</sup>	- 37
		S <sub>2</sub> O <sub>8</sub> <sup>''</sup>	- 74

The data for silver compounds are given in Table III. The argentous compounds are all diamagnetic and give practically zero moment. No simple salts of bivalent silver are known, but stable complex salts containing the metal co-ordinated with nitrogenous organic bases have been described by Barbieri (*Gazzetta*, 1912, **42**, ii, 7; *Ber.*, 1927, **60**, 2424), Hieber and Muhlbauer (*Ber.*, 1928, **61**, 2149), and by Morgan and Burstall (*J.*, 1930, 2554). Preliminary work with tris- $\alpha\alpha'$ -dipyridyl argentic chlorate has shown that in this substance bivalent silver is paramagnetic (Morgan and Sugden, *Nature*, 1931, **128**, 31). Professor Morgan and Mr. Burstall have generously placed the whole series of dipyridyl complexes at the author's disposal so that Table III contains data for a range of bivalent silver complexes. In every case it is found that these salts are paramagnetic and that the moments are of the same order of magnitude as those of bivalent copper. This result provides strong evidence for the view that the bivalency of the complex is due to the presence of a bivalent silver ion and not to incomplete co-ordination of the nitrogen atoms which might leave one of them free to function as a base.

It is noteworthy that the compounds in which silver has the co-ordination number 6 (Nos. 39-42) give a distinctly higher value of  $\mu$ . An attempt was made to examine argentic oxide, prepared as described by Austin (*J.*, 1911, **99**, 262), but the products obtained varied in composition and were all diamagnetic. This substance is being further investigated.

TABLE III.

*Silver Compounds.*

No.	Substance.	Ob-server.	t.	$\chi$ .	$\chi_M$ .	$\delta$ .	$\chi_A$ .	$\mu_m$
31	AgCl	M	17°	-0.66	-95	-20	-75	0
32	AgBr	,,	17	-0.61	-115	-31	-84	0
33	AgI	,,	17	-0.73	-172	-45	-127	0
34	AgNO <sub>3</sub>	S	20	-0.21	-36	-18	-18	0
35	[Ag 4py]NO <sub>3</sub>	,,	20	-0.25	-121	-206	81	0
36	[Ag 2dipy]NO <sub>3</sub>	,,	24	-0.46	-224	-220	-4	0
37	[Ag 4py]S <sub>2</sub> O <sub>8</sub>	,,	16	1.69	1041	-262	1303	1.74
38	[Ag 2dipy]S <sub>2</sub> O <sub>8</sub>	,,	23	1.83	1091	-276	1367	1.80
39	[Ag 3dipy](NO <sub>3</sub> ) <sub>2</sub>	,,	21	2.16	1512	-339	1851	2.09
40	[Ag 3dipy](ClO <sub>3</sub> ) <sub>2</sub>	,,	20	1.93	1434	-355	1789	2.05
41	[Ag 3dipy](ClO <sub>4</sub> ) <sub>2</sub>	,,	24	2.31	1790	-365	2155	2.16
42	[Ag <sub>2</sub> 5dipy](S <sub>2</sub> O <sub>8</sub> ) <sub>2</sub>	,,	24	2.03	2801	-653	1720	2.03

dipy =  $\alpha\alpha'$ -dipyridyl.

## EXPERIMENTAL.

*Preparation of Materials.*—A.R. Copper sulphate and silver nitrate were recrystallised, air-dried, and taken as pure. The copper derivatives of the  $\beta$ -diketones (Nos. 27—30) were recrystallised to constant melting point. Cuprous oxide was prepared by reducing excess of Fehling's solution with glucose and was dried in a vacuum over phosphoric oxide (Found: Cu, 85.8. Calc.: Cu, 88.87). Cupric oxide was prepared by ignition of the nitrate (Found: Cu, 79.2. Calc.: Cu, 79.9%).

Cuprous chloride, iodide, and thiocyanate were prepared by reduction of A.R. copper sulphate with sulphur dioxide and precipitation with the appropriate reagent; they were dried over phosphoric oxide (Found in CuCl: Cu, 63.7. Calc.: 64.2%. Found in CuI: Cu, 33.0. Calc.: 33.3%. Found in CuCNS: Cu, 51.9. Calc.: 52.3%).

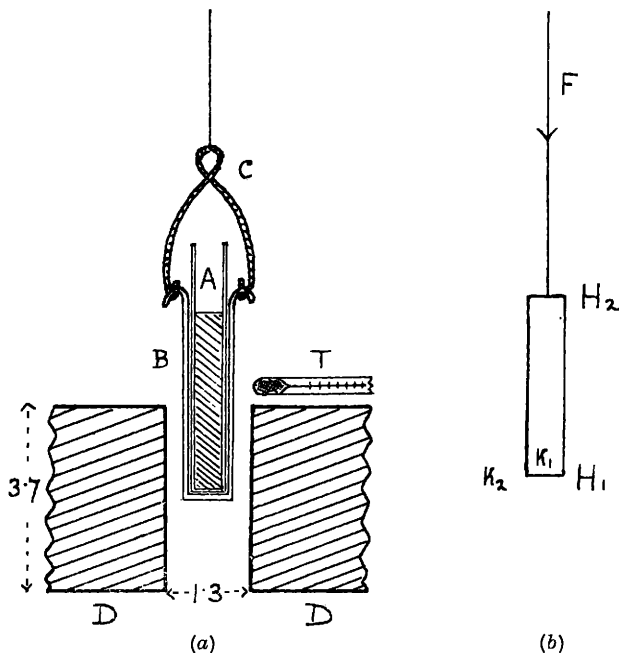
Tetrapyridine argentous nitrate (Found: Ag, 22.4. Calc. for [Ag 4py]NO<sub>3</sub>: Ag, 22.2%) was prepared by adding excess of pyridine to a concentrated solution of silver nitrate and was dried in a vacuum over caustic potash, m. p. 59° (Jørgensen, *J. pr. Chem.*, 1886, **33**, 502, obtained the dipyridine derivative of m. p. 87° by a similar reaction, but his product was dried over sulphuric acid). Tetrapyridine argentic persulphate was prepared as described by Barbieri (*loc. cit.*) and was dried in the same manner as the nitrate (Found: Ag, 17.5; S, 10.0. Calc.: Ag, 17.7; S, 10.4%).

For the preparation and analysis of the dipyridyl complexes, see Morgan and Burstall (*loc. cit.*).

*Determination of Magnetic Susceptibilities.*—For this purpose the Guoy method was chosen, in which one end of a column of the substance is suspended in a uniform magnetic field and the pull exerted by the field is measured. The experimental arrangement is shown

in Fig. 1(a). The stirrup of stiff brass wire *C* is suspended by a fine copper wire from the arm of a balance mounted on a shelf about a foot above the magnet. The stirrup supports a glass tube *B*, into which the experimental tube *A* slides loosely. The length of the suspension is adjusted so that the bottom end of *A* is at the centre of the gap between the wrought iron pole-pieces *D*. These were of square cross-section and had the dimensions shown in the diagram. This arrangement facilitated the removal and replacement of the tube *A* and ensured that the lower end of the column

FIG. 1.



of substance was always in the centre of the gap. The magnet coils had 3000 turns, and with a current of 3 amps. gave a field of the order of 3600 gauss.

In carrying out an experiment, the tube *A* was packed as uniformly as possible with the powdered substance to a fixed height and was placed in position. Screens were then erected to protect the tube from draughts and the apparatus left for 20 mins. to attain room temperature. The thermometer was then read and the weight of the tube accurately determined by the method of swings. The current was then switched on and the change in weight determined. As a check, the current was switched off and the weight

redetermined; this usually did not differ from the first observation by more than 0.1 mg. Blank experiments with the empty tube showed that it was feebly paramagnetic and gave a pull of 0.20 mg.; this weight was subtracted from the pull observed with the tube full.

The theory of the method may be briefly described as follows. In Fig. 1(b) let  $A$  be the cross-sectional area of the column of substance,  $\kappa_1$  its volume susceptibility,  $\kappa_2$  the susceptibility of the atmosphere, and  $H_1$  and  $H_2$  the field at the lower and the upper end respectively; then the pull exerted on the cylinder is

$$F = \frac{1}{2}A(\kappa_1 - \kappa_2)(H_1^2 - H_2^2) \text{ or } \kappa_1 = \kappa_2 + \frac{2F}{A(H_1^2 - H_2^2)} \quad (4)$$

Let  $w$  be the weight of substance and  $l$  the length of the column; then the density is  $d = w/LA$  and the mass susceptibility is given by

$$\chi = \frac{\kappa_1}{d} = \frac{\kappa_2 LA}{w} + \frac{2l}{(H_1^2 - H_2^2)} \cdot \frac{F}{w} \quad (5)$$

For the tube used,  $LA$  is 1 c.c., and  $\kappa_2$  for air is  $0.03 \times 10^{-6}$ ; hence (5) reduces to

$$10^6 \chi = 0.03/w + \alpha F/w \quad (6)$$

where  $\alpha$  is a constant for the apparatus, which can be determined by observations on suitable standard substances.

The constancy of  $\alpha$  depends, however, on that of  $H_1$  and  $H_2$ . With suitable pole-pieces, it is easy to ensure that  $H_1$  is constant for several mm. on either side of the centre of the gap. Since the weighing is made by swings, the experimental tube must move a little about its mean position; this effect was minimised by limiting the extent of the swings, but as  $H_2$  varies rapidly with distance from the centre of the gap it is evident that serious errors can arise if the column of substance is so short that  $H_2^2$  has an appreciable magnitude compared with  $H_1^2$ . To eliminate this error, the field was explored by using a tube filled with a long (10 cm.) column of copper sulphate. It was found that the field was uniform for 5 mm. above and below the centre of the gap, *i.e.*,  $H_1$  is constant, and became negligibly small compared with  $H_1$  at 4 cm. above the centre point. The length of the column of material in the experimental tube was therefore fixed at 4.5 cm.

An ammeter and variable resistance were included in the circuit of the magnet, and the influence on the field of change in current investigated. It was found that at 3 amps. the iron core was almost saturated and that increasing the current to 4 amps. gave only 5% increase. The current was therefore fixed at  $3.00 \pm 0.05$  amps.



for all subsequent experiments, as this gave a field of sufficient intensity without undue heating of the coils.

As magnetic standards for calibration, the following substances were chosen, since their susceptibilities have been accurately determined by Jackson (*Phil. Trans.*, 1924, *A*, **224**, 1):

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	$\chi_{16.6} = 41.46 \times 10^{-6}$ ; $\theta = -1^\circ$
$(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$	$\chi_{17.3} = 32.57 \times 10^{-6}$ ; $\theta = -1^\circ$
$(\text{NH}_4)_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	$\chi_{13.5} = 10.68 \times 10^{-6}$ ; $\theta = -4^\circ$

The specimens used were of A.R. quality and were recrystallised and air-dried. Details of the calibration experiments are given in Table IV.

TABLE IV.  
*Calibrations.*

Substance.	$t$ .	$\chi$ .	$w$ .	$F$ .	$\alpha$ .
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ .....	$20^\circ$	40.98	1.317	82.8	0.651
"  "	19	41.12	1.481	92.4	0.659
$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ .....	19	32.38	1.350	65.3	0.669
"         "  "	21	32.16	1.350	64.6	0.671
$\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ .....	21	10.40	1.267	20.0	0.657
"         "  "	25	10.27	1.153	18.1	0.652
				Mean	0.660

The mean value of  $\alpha$  was then used to calculate  $\chi$ . Thus, for copper acetylacetonate at  $16^\circ$ ,  $w = 0.896$  g.,  $F = +8.00$  mg. Hence  $10^6\chi = 0.03/0.896 + (0.660 \times 8.00)/0.896 = 5.92$ , or  $\chi = 5.92 \times 10^{-6}$ .

The value of  $F$  could be determined to 0.05 mg.; this corresponds to an error of  $0.03 \times 10^{-6}$  in  $\chi$ . Of other sources of error the most important seems to be that due to uneven packing of the material in the tube. To minimise this the powdered substance was rammed into the tube with a closely fitting glass rod in successive small quantities each sufficient to give a layer about 3 mm. high. Since equation (6) involves the ratio  $F/w$ , it is evident that small local variations in the density of the column will only give an error of the second order in  $\chi$ . In support of this view it was found that experiments in which the substance was lightly or heavily packed (compare the data for ferrous sulphate in Table IV) gave a constant ratio  $F/w$ .

#### Summary.

(1) The magnetic susceptibilities of 10 compounds of copper and 9 compounds of silver have been measured at room temperature.

(2) From these and other data in the literature, it is found that both copper and silver in the univalent condition have zero magnetic moment, whilst the bivalent atoms of these elements exhibit moments of 1.72—2.16 Bohr units, in fair agreement with the value predicted for one unbalanced electron.

Since this paper was written Klemm (*Z. anorg. Chem.*, 1931, 201, 33) has published data for the susceptibility of  $[\text{Ag } 4\text{py}]\text{S}_2\text{O}_8$ ,  $\chi_{\text{M}} = + 1200 \times 10^{-6}$ , and for  $[\text{Ag } 2(o\text{-phenanthroline})]\text{S}_2\text{O}_8$ ,  $\chi_{\text{M}} = + 1100 \times 10^{-6}$ . The first figure is 16% higher than the value found by the author, but both results are of the right order of magnitude for a substance containing an element with unit (Bohr) magnetic moment. Klemm finds that argentic oxide,  $\text{AgO}$ , is feebly paramagnetic, whilst the author has so far only obtained diamagnetic specimens.

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