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Electronic Constitution of Some Simple and Complex Derivatives of Copper in Relation to their Magnetic Properties.

By

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Abstract

1. The magnetic susceptibilities of 13 compounds of copper have been determined in solution and in the solid state.

2. It has been shown that the copper compound, in which the central metallic atom or ion contains completed sub-groups, possesses zero magnetic moment and is diamagnetic, whilst those in which the sub-groups are incompletely filled are paramagnetic.

In the formation of a co-ordination compound, according to Sidgwick (Jour. Chem. Soc., 1923, 123, 725), the central atom tends to assume the electronic configuration of the next higher inert gas, the co-ordinated atoms, groups or molecules being held by covalencies to the central nuclear atom. His view has been supported by Lowry (Jour. Soc. Chem. and Ind., 1923, 42, 316), Fowler (Discussion—Faraday Soc., "Electronic Theory of Valency," 1923) and Spiers (Jour. Soc. Chem. & Ind., 1923, 42, 534) and its importance has been revealed by Welo and Baudisch ("Nature," 1925, 116, 606), and Bose (Phil. Mag., 5, 1048, 1928).

Welo and Baudisch have brought into prominence the fact that the complex compounds whose 'effective atomic number,' is equal to that of the next higher inert gas exhibit diamagnetism as they form closed configurations like that of the latter. They also showed that complex compounds whose 'effective atomic number' falls short of or increases the inert gas configuration exhibit paramagnetism. Bose has gone a step forward and assumes that the magnetic moments of complex salts expressed in terms of Bohr's magneton are mostly proportional to the difference between their 'effective atomic number' and the atomic number of the next higher inert gas. Both these rules afford considerable support to the Sidgwick concepts of the structure of a co-ordination compound.

The magnetic properties of compounds, thus depend on the electronic configuration of the central atom. 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.

Magnetic susceptibilities of some simple and complex derivatives of copper have been determined in this investigation with a view to elucidate their electronic constitution.

Experimental.

The copper compounds were prepared by the well-known methods.

1. The copper salts of fatty acids—copper acetate, copper propionate, copper butyrate, copper valerate, copper caproate—were prepared by neutralising the corresponding acids with copper carbonate.

2. The copper derivatives of β-diketones were obtained by the methods whose references are given separately in each case.

(*a*) Copper acetyl acetonate. Jour. Chem. Soc., 1914, 105, 196.

(*b*) Copper benzoyl acetonate. Beilstein. VII, p. 769.

(*c*) Copper salt of aceto-acetic ester, Ber., 1898, 31, 3153.

(*d*) Copper dimethyl glyoxime. "Collection," 1929, p. 151.

3. The complex derivatives of copper stabilised by ethylene diamine-bisethylene diammino-cupric nitrite, bisethylene diammino-cupric thiosulphate, bisethylene diammino-cupric hypophosphite were prepared according to the methods of Morgan and his co-workers (Jour. Chem. Soc., 1926, pp. 2018-2027 and 1927, p. 1264).

Tetra-kis-ethylene thio-carbamido cuprous nitrate was very kindly supplied by Prof. G. T. Morgan of the National Physical Laboratory, for which we are very highly grateful to him.

Magnetic susceptibilities of the copper salts, in solution were determined by the Quincke's method. Mass susceptibility of the solute was then calculated in each case by the application of Wiedemann's law (Pogg. Ann., 1865, 1, 126, and Jour. Amer. Chem. Soc., 1926, 48, 847).

The results obtained in solution by the Quincke's method were further verified by finding out magnetic susceptibilities of the copper salts in the soild state [1] by the Guoy's method modified by Bhatnagar, Mathur and Kapur (Indian Jour. Phys., 1928, 3, 56). From the magnetic susceptibility values of the copper salts, (p) Weiss magnetons were calculated in each case and the results are given in the following table.

[1] Some of the observations in the soild state were made by Mr. P. L. Kapur for which we are thankful to him.

TABLE I.

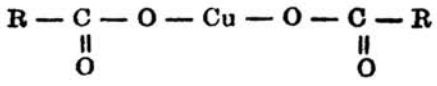
Substance.	Mass Susceptibility. $\chi_m \times 10^6$.		Molecular Susceptibility. $\chi_M \times 10^6$.		Curie Constant. C_M.		Weiss Magneton p.		Mean. p.
	Quincke.	Guoy.	Quincke.	Guoy.	Quincke.	Guoy.	Quincke.	Guoy.	
Copper acetate	7·614	7·418	1520	1481	0·4605	0·4486	9·5	9·4	9·5
Copper propionate	6·054	6·704	1379	1527	0·4186	0·4626	9·1	9·6	9·4
Copper butyrate	5·624	6·046	1438	1546	0·4356	0·4793	9·3	9·7	9·5
Copper valerate	5·117	5·248	1359	1394	0·4118	0·4223	9·0	9·1	9·1
Copper caproate	4·905	5·089	1441	1495	0·4364	0·4529	9·3	9·5	9·4
Copper acetyl acetonate.	5·645	5·828	1477	1521	0·4482	0·4608	9·4	9·6	9·5
Copper benzoyl acetonate.	3·710	3·785	1431	1460	0·4357	0·4422	9·3	9·4	9·4
Copper salt of acetoacetic ester.	4·790	5·135	1540	1650	0·4668	0·4989	9·6	9·9	9·8
Copper dimethyl glyoxime.	4·912	5·577	1448	1676	0·4371	0·5078	9·3	10·0	9·7
Bisethylene diammino cupric nitrite.	5·837	6·198	1609	1700	0·4875	0·5174	9·8	10·1	9·9
Bisethylene diammino cupric thiosulphate.	5·295	6·413	1567	1605	0·4732	0·4863	9·7	9·8	9·8
Bisethylene diammino cupric hypophosphite.	5·115	5·212	1604	1685	0·4862	0·4955	9·8	9·9	9·9

Tetra-kisethylene thio-carbamido cuprous nitrate is found to be diamagnetic and its specific susceptibility determined by Wilson's balance is $-0{\cdot}55 \times 10^{-6}$.

Discussion.

According to Sidgwick ("The Electronic Theory of Valency," p. 254), the cupric derivatives of fatty acids are not

chelate compounds but exist in a covalent form.



In this investigation these compounds are found to be paramagnetic and their (p) Weiss magneton values vary from 9 to 10 units. The magnetic moment of a molecule is due to spin moments of unpaired electrons. Thus the cupric ion in these compounds contains an incomplete sub-group and its electronic structure is represented as

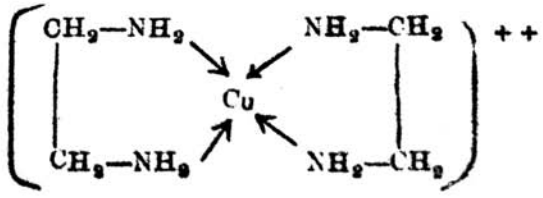
$$Cu^{++}\ 2,\ 224,\ 22445$$

The paramagnetism exhibited by these compounds is, therefore, due to the incomplete electronic M_{33} sub-group of the central metallic atom.

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 (*loc. cit.*). They 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.

The ' effective atomic number ' in case of the cupric derivatives of β-diketones and dimethyl glyoxime is equal to $35(29+1\times 2+2\times 2=35)$, as calculated according to Sidgwick's rules (The Electronic Theory of Valency, p. 163).

With ethylene diamine, copper forms a co-ordination complex having the following structure :

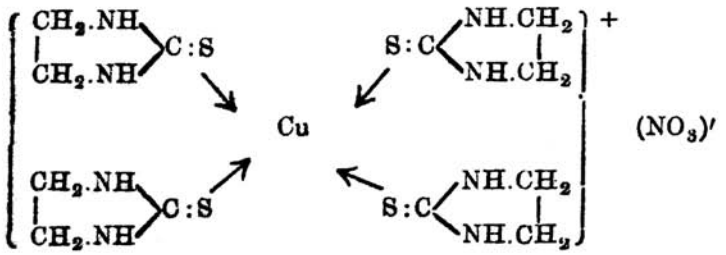


The central metallic atom is co-ordinated with two molecules of the base (ethylene diamine) and its effective atomic number is equal to $35(29+2\times4-2=35)$.

Thus the copper derivatives of β-diketones, dimethyl glyoxime and ethylene diamine are four-fold co-ordination compounds having 35 as the 'effective atomic number' of the central metallic atom. The electronic structure of the co-ordinated copper atom is represented as 2, 224, 22445, 224 which differs from the arrangement 2, 224, 22446, 224 for krypton, the next inert gas, in a shortage of one electron in the ninth (M_{33}) sub-group. According to Welo and Baudisch and Bose such compounds should exhibit paramagnetism.

In this investigation copper acetyl acetonate, copper benzoyl acetonate, copper salt of aceto-acetic ester, copper dimethyl glyoxime, bisethylene diammino cupric thiosulphate, bisethylene diammino cupric nitrite and bisethylene diammino cupric hypophosphite are all experimentally found to be paramagnetic in accordance with the theory. These observations, therefore, confirm the structure assigned to the copper complex compounds.

In tetrakisethylene thiocarbamido-cuprous nitrate, (Cu. 4 etu) NO_3, which may have the following structure :—



the cuprous ion is eight electrons short of the number required for the krypton structure, but by becoming co-ordinated with four molecular proportions of cyclic thio-base (ethylene thiocarbamide etu) it acquires these additional electrons. In

other words its 'effective atomic number' calculated according to Sidgwick's rules would become equal to 36; because each of the ethylene thio-carbamide molecule adds two electrons and the $(NO_3)'$ radical attached to the complex by an electrevalent link, removes one electron thus leaving the total number of electrons associated with the central copper atom equal to 36 ($29 + 2 \times 4 - 1 = 36$).

The number of electrons associated with the central copper atom in the complex is thus the same as the number in the inert gas atom krypton, and presumably forms a closed configuration of the inert gas type, with a zero magnetic moment. It has been verified experimentally as the complex compound is found to be diamagnetic.

The influence of co-ordination upon magnetic moment in case of the complex compounds of copper studied in this investigation is summarised in the following table.

TABLE II.

Compound.	Co-ordination number.	Effective Atomic Number.	Magnetic Moment.	
			Weiss Magnetons.	Bohr Magnetons.
Copper acetyl acetonate ...	4	35	9·50	1·91
Copper benzoyl acetonate ...	4	35	9·35	1·88
Copper salt of aceto-acetic ester ...	4	35	9·75	1·96
Copper dimethyl glyoxime ...	4	35	9·65	1·94
Bisethylene diammino cupric thio-sulphate	4	35	9·75	1·96
Bisethylene diammino cupric nitrite	4	35	9·90	1·99
Bisethylene diammino cupric hypo-phosphite	4	35	9·85	1·98
Tetrakisethylene thio-carbamido cuprous nitrate	4	36	0·0	0·0

The values of the magnetic moments in Bohr magnetons for the above compounds are in accordance with Bose's rule $(Z-Z' = n)$ where (Z) is the atomic number of the next inert gas, (Z') the effective atomic number of the co-ordinating atom and (n) the number of Bohr magnetons.

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