Magnetic Susceptibilities of Some Square Four-Covalent and Tetragonal Six-Covalent Complexes of Divalent Copper

C. Djordjević

*Department of Structural and Inorganic Chemistry,
Institute »Ruđer Bošković«, Zagreb, Croatia, Yugoslavia*

Received September 30, 1960

Measurements of the magnetic susceptibility of some tetra-coordinated square planar cupric compounds of the type $[Cu(NH_3)_4]X_2$, $X=NO_3^-$, NO_2^-, CNS^-, $SO_4^=$ and hexa-coordinated complexes of the type $[Cu(NH_3)_6]X_2$, $X = Cl^-$, Br^-, I^-, have been carried out at room temperature. The complexes $Cu(AcAc)_2$ and $Cu(AcAc)_2 \cdot 2NH_3$ have also been examined.

It has been found that there is no significant difference in the orbital contribution between the planar tetra-coordinated and tetragonal hexa-coordinated compounds. The values of the magnetic moments at room temperature are of the order of 1.80 and 1.96 B. M., regardless of the stereochemical arrangement of the investigated complexes.

INTRODUCTION

It is of interest to know whether it is possible to deduce a qualitative picture for the stereochemistry of cupric compounds from a simple determination of the magnetic moment. The first step in such an investigation is to find a correlation between the coordination number, stereochemistry and orbital magnetism for a series of four-, five- and six-coordinated cupric complexes.

The stereochemistry of the cupric compounds is unusual. The regular octahedral environment of Cu^{II} occurs rarely — if ever. Three coordination types have been found: the square planar, tetragonal (distorted octahedral) and tetrahedral. Only a few tetrahedral complexes are known[1], the first and the second type comprising the vast majority of the cupric compounds.

Wells[2] suggested that the odd 4 p electron may be responsible for the two additional weak bonds. However, the presence of an odd 4 p electron is incompatible with the recent evidence obtained from paramagnetic resonance[3,4] and optical studies[5,6]. It is also difficult to accept Wells's explanation because of the marked resistance of the cupric ion to further oxidation. The stereochemistry of the cupric complexes can be understood in terms of the Jahn--Teller effect outlined by Orgel[7,8]. According to this picture the cupric compounds are regarded as retaining their full complement of nine 3 d electrons. The observed stereochemical features are related to distortions of the Jahn--Teller type, because the ground state of the cupric ion is orbitally degenerate.

Several authors have reported measurements of magnetic properties of cupric compounds, mostly at room temperature only[9,10]. It has been shown that under condition of adequate magnetic dilution, the cupric ion exhibits a mo-

ment somewhat above the »spin-only« value for the one unpaired electron configuration of d^9, *i.e.* 1.73 B. M.

Ray and Sen[11] had earlier claimed to have obtained a correlation between colour, orbital contribution and stereochemistry, but they gave for many compounds high values of the Weiss-constant ($\theta \cong 100^0$). Later, Figgis and Harris have shown[12] that the measurement of the susceptibility of some cupric compounds over a range of temperature gives olny very small values of θ. ($\theta \cong 9^0$). The higher values of the magnetic moments therefore cannot be explained on the basis of the high values of θ.

In this investigation a series of cupric complexes of the type $[Cu(NH_3)_4]X_2$, $[Cu(NH_3)_6]X_2$, $Cu(AcAc)_2$ and $Cu(AcAc)_2$ $2NH_3$ has been prepared. Measurements of the magnetic susceptibility at room temperature have been carried out in order to find the orbital magnetism and its possible dependence upon the stereochemical arrangement.

EXPERIMENTAL

I. Preparation of the compounds

The hexammino- and pentammino-cupric compounds have been prepared (with slight modifications) according to the method of Ephraim[13], Biltz[14], and Peyronel[15]:

1) *[Cu(NH₃)₆]Cl₂*

Anal. Found: Cu, 28.6; NH₃, 39.7; Cl, 31.9.

The experimental analytical figures indicate that the complex is not a pure hexammino-compound at room temperature. The analysis is equally consistent with the following mixtures: 81% pentammino- and 19% hexammino- complex, or 61% tetrammino and 39% hexammino-complex. (81% pentammino-complex requires: Cu, 28.6; NH₃, 39.5; Cl, 31.9. 61% tetrammino-complex requires: Cu, 28.6; NH₃, 39.5; Cl, 31.9.) It is also possible, that at room temperature a mixture of all the three components is present: hexammino-, pentammino- and tetrammino-cupric complexes.

2) *[Cu(NH₃)₆]Br₂*.

Anal. Found: Cu, 20.1; NH₃, 29.5; Br, 50.4.

The analytical data indicate again an equillibrium mixture, as for the above mentioned chloride. The substance obtained at room temperature corresponds equally well to a mixture of 54.5% pentammino- and 45.5% hexammino-complex, or 74% hexammino- with 26% tetrammino-complex. (54.5% pentammino-complex requires: Cu, 20.1; NH₃, 29.4; Br, 50.5. 26% tetrammino-complex requires: Cu, 20.1; NH₃, 29.3; Br, 50.7.) A mixture of all the three components may also be present.

3) *[Cu(NH₃)₆]I₂*. The analysis correspond well to the hexammino-complex at room temperature. Calculated for Cu(NH₃)₆I₂: Cu, 15.1; NH₃, 24.4. Found: Cu, 15.1; NH₃, 24.8.

4) *[Cu(NH₃)₄] (NO₃)₂* was prepared by the conventional method described by Mellor[16]. (Formula requires: NH₃, 26.6; found: 26.7).

5) *[Cu(NH₃)₄] (NO₂)₂* was prepared according to King's method[18]. (Formula requires: Cu, 28.4; found: 28.4).

6) *[Cu(NH₃)₄]SO₄* was prepared from anhydorus cupric sulphate and ammonia[17]. (Formula requires: Cu, 27.9; found: Cu, 27.5).

7) *[Cu(NH₃)₄] (CNS)₂* was prepared according to the literature[19]. (Formula requires: Cu, 25.7; found: 25.2).

8) *Cu(AcAc)₂* was prepared from cupric acetate and acetylacetone and recrystallised from toluene. (CuC₁₀H₁₄O₄ requires: Cu, 24.3; C, 45.9; H, 5.4; found: Cu, 24.3; C, 45.7; H, 5.4).

9) *Cu(AcAc)₂ · 2NH₃* was prepared by treating cupric acetylacetonate with liquid ammonia. After evaporation of the excess of ammonia, a pale green substance was obtained. The complex is stable only in the atmosphere of ammonia. (Formula requires: Cu, 21.5; found: 21.5).

II. *Measurements of the magnetic susceptibility*

Magnetic susceptibility measurements were made on powders, using the Gouy method. A permanent magnet was used, having an interpole gap of 5/8'' and a field strength of about 7000 Gauss. Analar copper sulphate pentahydrate (gram susceptibility = $5.92 \cdot 10^{-6}$ C. G. S. units at 19°C) was used to calibrate the tube. For temperatures up to 25°C the susceptibility of the copper sulphate was calculated using a Curie Law. The value found for the gram susceptibility (χ_g) was then converted to molar susceptibilities (χ_M) and finally corrected for diamagnetism of the ligands and anions. The corrected χ_M value was used to calculate the effective magnetic moment (μ_{eff}) of the metal atom concerned by the formula $\mu_{eff} = 2.84 \sqrt{\chi_M T}$, where T is the absolute temperature. The number, n, of unpaired electrons in the atom was then computed by comparing the theoretical spin-only value for μ_{eff} given by the formula $\mu_{eff} = \sqrt{n(n+2)}$.

Because of the extremely unstable character of the complex $Cu(AcAc)_2 NH_3$, an arrangement was made to transfer the substance to the Gouy and measure the magnetic moment in the atmosphere of ammonia.

Values of the magnetic moments obtained in this way are listed in Table I.

RESULTS AND DISCUSSION

In order to find the change in the orbital contribution between square four-covalent and tetragonal six-covalent complexes of divalent copper, the compounds listed in Table I were prepared and the magnetic susceptibility was measured at 25°C.

TABLE I

Compound	Magnetic Moment in Bohr Magnetons
$[Cu(NH_3)_5]Cl_2$	1.80 B. M.
$[Cu(NH_3)_{5,6}]Br_2$	1.85 B. M.
$[Cu(NH_3)_6]I_2$	1.95 B. M.
$[Cu(NH_3)_4] (NO_3)_2$	1.83 B. M.
$[Cu(NH_3)_4] (NO_2)_2$	1.84 B. M.
$[Cu(NH_3)_4] (CNS)_2$	1.81 B. M.
$[Cu(NH_3)_4]SO_4$	1.80 B. M.
$Cu(C_5H_7O_2)_2$	1.96 B. M.
$Cu(C_5H_7O_2)_2 \cdot 2NH_3$	1.93 B. M.

The observed magnetic moments in Table I are of the order 1.80—1.96 B. M. From the given values it is obvious that there is very little change in the orbital contribution between square and tetragonal cupric complexes. According to Ephraim[13] and Blitz[14] the amount of ammonia bound in the complexes of the type $[Cu(NH_3)_6]X_2$ is greatly dependent on temperature, and there is a range of mixed crystals formed between the hexa- and pentammines. The chloride and the bromide complexes are at room temperature (see Experimental) a mixture of two or even three components (hexammino-, pentammino-, and tetrammino-complexes). For the iodide (see Experimental) the empirical formula at 25°C corresponds exactly to a hexammine. There are no full structural analyses available for cupric tetrammino and hexammino complexes. Peyronel[15] has found that cupric hexammine bromide and iodide are isomorphous, both having a cubic structure. The chloride is not isomorphus with them. From his investigations Peyronel concluded that hexammines of divalent copper have an octahedral coordination, which is regular in the bromide and iodide. He

assumes that in the case of chloride the distortion of the molecule causes the loss of the cubic structure. However, this evidence is not conclusive and small increase in bond distances would not show in his experimental data. One would expect the tetragonal distortions of the octahedral arrangements to increase from chloride through bromide to iodide, because of the increased polarisability (decreased electronegativity) of the anion. This may not affect the crystal structure in the least, particularly if there is in the solid state an equilibrium of mixed phases, owing to the temperature dependent content of ammonia. The magnetic moment of the complex $[Cu(NH_3)_6]I_2$ shows a slight increase in agreement with the above discussion, but the difference is insignificant. There is virtually no difference in magnetic moments of the tetrammine and hexammine complexes.

Figgis and Harris[12] have found that magnetic moments of a number of cupric compounds are essentially independent of temperature. They discuss their results in cupric complexes with regard to stereochemistry and bond type in terms of spectroscopic properties of the metal ion. The high values of the magnetic moments (of the order of 2.0 B. M.) are explained by a fairly large spin-orbit coupling constant of the Cu^{2+} ion ($A = 852$ cm^{-1}), as shown by Polder[20]. The moment for an octahedral complex is given by the spin-only value of 1.73 B. M. multiplied by the factor ($1 + 2 A/\Delta$). In this formula Δ is the ($d_\varepsilon - d_\gamma$) separation. For the tetragonal distortion of the octahedral case, or a square planar complex the significance of Δ in the expression $\mu = \mu_{\text{spin only}}$ ($1 + 2 A/\Delta$) is then the separation between the $d_{x^2-y^2}$ and d_{xz} and d_{yz} orbitals. For the tetrahedral stereochemical arrangement the ground state of the ion would be more complicated and lead to a more complicated magnetic behaviour than in the octahedral case.

The observed moments in Table I are therefore consistent with this theory. The values at room temperature are of the order 1.8—1.96 B. M. and the stereochemistry of the compounds probably varies from square planar to tetragonally distorted octahedral arrangements. It is not possible to distinguish between the planar and tetragonal cupric compounds on the basis of the magnetic susceptibility data.

REFERENCES

1. G. Felsenfeld, *Proc. Roy. Soc. (London), (A)* **236** (1956) 506.
2. A. F. Wells, »*Structural Inorganic Chemistry*«, Oxford Univ. Press, Oxford, 1950.
3. B. Bleaney and K. W. H. Stevens, *Reports Progr. Phys.* **16** (1953) 108.
4. K. D. Bowers and J. Owen, *ibid.* **18** (1955) 304.
5. J. Bjerrum, *Acta Chem. Scand.* **8** (1954) 1275.
6. L. E. Orgel, *J. Chem. Phys.* **23** (1955) 1004.
7. L. E. Orgel, *Report on the 10th Solvay Council*, Brussels, 1956, 289.
8. L. E. Orgel and J. D. Dunitz, *Nature* **179** (1957) 462.
9. C. Djordjević, *Thesis*, University College, London, 1959.
10. P. Lumme, *Suomen Kemistilehti* **32** (1959) 203.
11. P. Ray and D. N. Sen, *J. Indian Chem. Soc.* **25** (1948) 473.
12. B. N. Figgis and C. M. Harris, *J. Chem. Soc.* **1959**, 855.
13. F. Ephraim, *Ber.* **52** (1919) 940.
14. W. Biltz, *Z. Anorg. Allgem. Chem.* **148** (1925) 207.

15. G. Peyronel, *Gazz. Chim. Ital.* **71** (1941) 363.
16. J. W. Mellor, *»A Comprehensive Treatise on Inorganic and Theoretical Chemistry«*, Longmans, 1923, Vol. III., p. 284.
17. J. W. Mellor, *ibid.*, p. 251.
18. H. J. S. King, *J. Chem. Soc.* **1929**, 2593.
19. Gmelin Kraut's *»Handbuch der Anorganischen Chemie«*, Carl Winter's, Heidelberg, 1909, Band V., Abt. 1., p. 1030.
20. D. Polder, *Physics* **9** (1942) 709.

IZVOD

Magnetski susceptibilitet nekih planarnih tetra-koordiniranih i tetragonskih heksa-koordiniranih kompleksa dvovalentnoga bakra

C. Djordjević

Izvedena su mjerenja magnetskoga susceptibiliteta tetra-koordiniranih planarnih i heksa-koordiniranih tetragonskih kupri-kompleksa tipa $[Cu(NH_3)]_4X_2$, $X = NO_3^-$, NO_2^-, CNS^-, $SO_4^=$ i $[Cu(NH_3)_6]X_2$, $X = Cl^-$, Br^-, J^-. Istraživani su osim toga i kompleksi $Cu(AcAc)_2$ i $Cu(AcAc)_2 \cdot 2NH_3$.

Utvrđeno je, da nema značajne razlike u orbitalnom magnetizmu između planarno-tetra-koordiniranih i tetragonsko-heksa-koordiniranih kompleksa. Vrijednosti magnetskog momenta kod sobne temperature kreću se između 1.80 i 1.96 B. M., te ne pokazuju ovisnost o stereokemijskom tipu istraživanih kompleksa.

ODJEL STRUKTURNE I ANORGANSKE KEMIJE
INSTITUTA »RUĐER BOŠKOVIĆ«
ZAGREB