175. *Magnetochemistry. Part III.* Compounds of Bivalent Copper.*

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The temperature dependence of the magnetic susceptibility of 9 cupric co-ordination compounds is reported over the temperature range 80—300° K. The significance of the results is discussed with regard to stereochemistry and bond type in cupric complexes. It is found that the magnetic moments of 1·8—2·0 B.M. at room temperature are essentially independent of temperature.

There have been many measurements of the magnetic properties of bivalent copper compounds, mostly at room temperature only. It seems well established that, under conditions of adequate magnetic dilution the cupric ion exhibits a moment somewhat above the spin-only value for the one unpaired electron configuration of d^9, *i.e.*, 1·73 B.M. This is as expected for the cupric ion, at least if the ligand distribution around it is essentially octahedral. However, a number of points need clarification, particularly in regard to the stereochemistry and bonding of the cupric ion.

Ray and Sen [1] reported the moments at room temperature and, in some instances, at unspecified lower temperatures, of a number of typical cupric co-ordination complexes. They correlate the magnetic moments of 1·7—1·9 B.M. on the one hand with a red-yellow colour, and of 1·9—2·2 B.M. on the other with a green-blue colour. They attribute to the latter group a tetrahedral stereochemistry of the attached ligands on the grounds that such an arrangement might well lead to higher moments than does the octahedral arrangement of the ligands which they assigned to the former group. The larger moments reported by Ray and Sen were often associated with very high values of θ, the Weiss constant in the Curie-Weiss law, of up to 100°. The moments they found were calculated by means of the expression $\mu'_{\text{eff}} = 2{\cdot}84\sqrt{[\chi_{\text{Cu}}(T + \theta)]}$. When calculated as $\mu_{\text{eff}} = 2{\cdot}84\sqrt{(\chi_{\text{Cu}}T)}$, moments higher than 2·0 B.M. are not observed at room temperature. In no case, other than for some distorted octahedral arrangements, was the stereochemistry certain. These high values of θ are at variance with the other available data on cupric compounds, and are difficult to understand when they occur in complexes of octahedral stereochemistry. We have repeated the measurements of the susceptibility over a range of temperature for two of the compounds concerned, Cu(dimethylglyoxime)Cl_2 and Cu(glycine)$_2$,H_2O, and find very small values of θ in place of ~100°. It may be that such high values of θ are due to the lack of magnetic dilution, as in the acetate [2] and formate [3] of copper, but this is unlikely and would invalidate all but the most careful arguments based on the moments to which they pertain.

As shown in Fig. 1, the Cu^{2+} ion gives rise to a ^2D spectroscopic state which is split by an octahedral crystalline field into an upper orbital triplet (d_ϵ) and a lower lying " non-magnetic " doublet (d_γ). The separation is ~10,000—20,000 cm.$^{-1}$. The term " non-magnetic " has been used [4] to emphasise the fact that these levels cannot by themselves form part of the orbital contribution to the moment in spite of their orbital degeneracy; it does not apply to the spin contribution to the moment which these levels may make. The green-blue colours frequently observed for cupric complexes can be attributed to transitions between the d_γ–d_ϵ ligand field levels, and have values of $\varepsilon_{\text{max.}}$ (extinction coefficient) of 10—100 consistent with this. The red, deeper-coloured complexes, on the

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* Parts I and II, *J.*, 1959, 331, 338.

[1] Ray and Sen, *J. Indian Chem. Soc.*, 1948, **25**, 473.

[2] Figgis and Martin, *J.*, 1956, 3837.

[3] Martin and Whitley, *J.*, 1958, 1394.

[4] Bethe, *Z. Physik*, 1930, **60**, 218.

other hand, appear to owe their colour to charge-transfer bands of $\varepsilon_{\text{max.}} \geqslant 1000$ at energies $\geqslant 20{,}000$ cm.$^{-1}$, *e.g.*, the $[CuCl_3]^-$ ion in nitrobenzene.[5]

In a tetrahedral complex the d_ϵ levels lie lowest. Although the d_γ levels cannot give rise to orbital contribution, there is, as Polder[6] has shown, a considerable interaction between the d_γ and d_ϵ levels by means of the fairly large spin–orbit coupling constant of the Cu^{2+} ion ($A = 852$ cm.$^{-1}$). This effect gives rise to the quite appreciable orbital contribution observed in the moment of, say, $CuSO_4,5H_2O$ (1·95 B.M.). A tetragonal ligand field is usually present in addition to the main one of cubic symmetry in " octahedral " cupric complexes; it arises from a lifting of the degeneracy of the d_γ^3 ground state by means of the Jahn–Teller effect with a consequent distortion of the octahedral ligand arrangement of small magnitude.[7] Polder invoked an improbably large tetragonal field distortion, a splitting of the d_γ levels of $\sim$10,000 cm.$^{-1}$, and considered only the case when the $d_{x^2-y^2}$ orbital contained the unpaired electron. However, Polder's explanation of the orbital contribution is independent of the magnitude of the tetragonal splitting or its sign provided that only the mean susceptibility, as distinct from the magnetic anisotropy, is considered. Whichever of the $d_{x^2-y^2}$ or d_{z^2} orbitals lies lowest, the moment is given by the spin-only value of 1·73 B.M. multiplied by the factor $(1 + 2A/\Delta)$, where Δ is the d_ϵ–d_γ separation. With $\Delta \sim$20,000 cm.$^{-1}$ a moment of about 1·88 B.M. is predicted for an octahedral complex. Since the d_γ levels are " non-magnetic " the ground level in an octahedral complex must be a spin (Kramer's) doublet or, if the d_γ levels are degenerate within kT, a mixture of two spin doublets of identical mean magnetic properties. Consequently, the magnetic susceptibilities of octahedral cupric complexes should follow the Curie law closely, as there is no mechanism for ground-state levels of different magnetic properties separated by $\sim kT$. This prediction is in keeping with most of the data on the magnetic behaviour of the cupric ion.

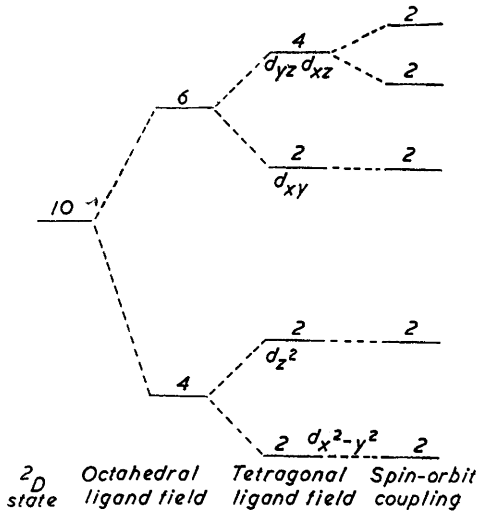

FIG. 1. *Splitting of the ^2D state of the cupric ion. The numbers above a level indicate the degeneracy to a magnetic field. The splitting by a tetragonal field component corresponds to the elongation of an octahedron in the z axis; it is reversed for a tetragonal component of the opposite sign.*

When the stereochemistry of the ligand distribution around the cupric ion ceases to be even approximately octahedral it is no longer possible to make accurate predictions about the magnetic properties of the ion in most cases. The extension of the tetragonal distortion of the octahedral case to the complete removal of one or two *trans*-ligands to leave a tetragonal pyramidal or a square planar complex is expected to change the magnetic

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[5] Nyholm, *J.*, 1951, 1767.

[6] Polder, *Physica*, 1942, **9**, 709.

[7] Dunitz and Orgel, *Nature*, 1957, **179**, 462.

properties comparatively little from those of octahedral complexes. The significance of Δ in the expression $\mu = \mu_{\text{spin-only}} (1 + 2A/\Delta)$ is then the separation between the $d_{x^2-y^2}$ and the d_{xz} and d_{yz} orbitals, as illustrated in Fig. 1 of Part II of this series.[8] When the stereochemistry is tetrahedral it might be expected, as suggested by Ray and Sen, that the ground state of the ion would be more complicated and lead to higher moments and more complicated magnetic behaviour than in the octahedral case. If there is no ligand field of lower than tetrahedral symmetry the magnetic behaviour should be similar to that of the octahedral d_ϵ^5 configuration, as set out by Kotani.[9,10] For Cu^{2+}, kT/A is about 0·25 at room temperature, and moments of about 2·2 B.M., together with some small departure from the Curie law, are predicted. However, it is likely that the degeneracy of the ground state in this case also would be lifted by a Jahn–Teller mechanism and this, in the form of a ligand field of lower symmetry, could lead to modified magnetic behaviour.

In order to try to clarify the position we have measured the susceptibilities of a number of cupric complexes of various types of stereochemistry over the temperature range 80—300° K. It was not possible to test in a satisfactory manner the considerations on the tetrahedral configuration, for there is only one compound available which is known with certainty to have even approximately that stereochemistry, *i.e.*, Cs_2CuCl_4, and it is not possible to generalise too far from a single example.

Discussion.—The results of the measurements which we have performed on the magnetic properties of cupric complexes are set out in the Table and Figs. 2—4. It is not certain in every case what the stereochemistry of the ligand distribution around the cupric ion is, for *X*-ray information on the structure is available in only some instances. However, the cases where this information is lacking are those where there seems to be no reason to doubt an octahedral or distorted octahedral arrangement. The striking feature of the results is that the moments all lie within the range 1·7—2·0 B.M. over the entire temperature range, and that the values of the Weiss constant, θ, are uniformly small—in no case above 9°.

Diamagnetic corrections, magnetic moments at 300° *and* 90° K, θ *values and accuracies of the measurements of relative susceptibilities at different temperatures for the compounds of bivalent copper studied.*

Compound	Colour	Diamagnetic corrn./ mole, × 10⁶	$\mu_{\text{eff.}}$ 90° K (B.M.)	$\mu_{\text{eff.}}$ 300° K (B.M.)	θ	Accuracy (%)
Cu(*o*-phenanthroline)$_3$(ClO$_4$)$_2$	Pale blue	395	1·96	1·91	−9°	1
Cu(dipyridyl)$_3$(ClO$_4$)$_2$	Blue	380	1·91	1·96	5	1
$CsCuCl_3$	Garnet	105	1·93	1·95	1	1
Cu(*o*-phenanthroline)$_2$Br(ClO$_4$)	Green-blue	280	1·68	1·72	8	0·5
Cu(*o*-phenanthroline)$_2$Br$_2$	Pale green	285	1·74	1·75	5	1
Cu(acetylacetone)$_2$	Blue	120	1·89	1·90	0	2
Cu(dimethylglyoxime)Cl$_2$	Deep green	170	1·84	1·85	4	2
Cu(*o*-phenanthroline)$_2$(ClO$_4$)$_2$	Green-blue	275	1·94	1·89	−7	1
Cs_2CuCl_4	Brown-yellow	165	1·99	2·00	1	1

The case of octahedral or almost octahedral symmetry has been the subject of most studies in the literature where the stereochemistry has been known for certain. The temperature dependence of the susceptibilities of numerous Tutton salts, where the ligand field is known to be cubic with a small trigonal component, have been reported;[11-13] θ is invariably small. Of the compounds reported in this work there seems to be no reason to doubt the octahedral stereochemistry of Cu(*o*-phenanthroline)$_3$(ClO$_4$)$_2$ and Cu(dipyridyl)$_3$(ClO$_4$)$_2$, particularly as the former is isomorphous with the nickel

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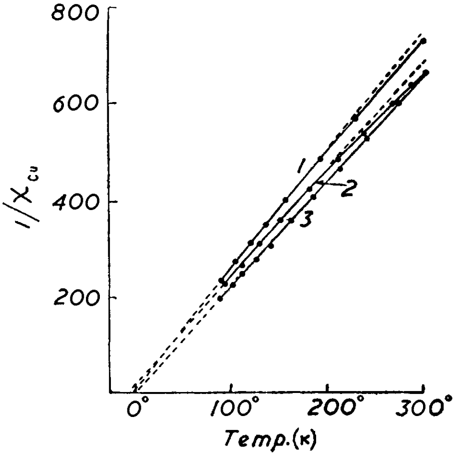
[8] Figgis and Nyholm, *J.*, 1959, 338.
[9] Kotani, *J. Phys. Soc. Japan*, 1949, **94**, 293.
[10] Cf. Earnshaw, Figgis, Lewis, and Nyholm, *Nature*, 1957, **179**, 1121.
[11] Krishnan and Mookherji, *Phil. Trans.*, 1938, *A*, **238**, 125.
[12] Hupse, *Physica*, 1942, **9**, 633.
[13] Bose, Datta, and Mitra, *Proc. Roy. Soc.*, 1957, *A*, **239**, 165.

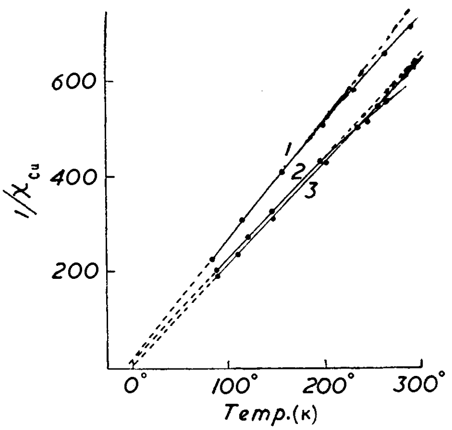
derivative.[14] The environment of the Cu^{2+} ion in $CsCuCl_3$ is known to be approximately octahedral from the *X*-ray structure determination.[15] Taken in conjunction with the well-established $\theta = 1°$ for $CuSO_4,5H_2O$ (see Part I [16]), it seems certain that the magnetic behaviour of the ground state of the cupric ion in an octahedral environment is very simple, in accord with the theory outlined above. The moments, at about 1·9 B.M., are close to those reported in refs. 11—13, and are in accord with the theory.

FIG. 2.



1, Cu(*o*-phenanthroline)$_3$(ClO_4)$_2$.
2, Cu(dimethylglyoxime)Cl_2.
3, Cu(acetylacetone)$_2$.

FIG. 3.



1, Cu(*o*-phenanthroline)$_2$$Br_2$.
2, Cu(dipyridyl)$_3$(ClO_4)$_2$.
3, $CsCuCl_3$.

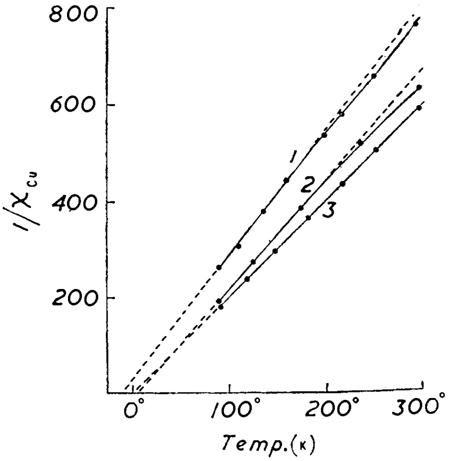


FIG. 4.

1, Cu(*o*-phenanthroline)$_2$Br(ClO_4)
2, Cu(*o*-phenanthroline)$_2$(ClO_4)$_2$.
3, Cs_2CuCl_4.

A stereochemistry of a distorted octahedral form is probably to be assigned to the compounds Cu(*o*-phenanthroline)$_2$$Br_2$ and Cu(*o*-phenanthroline)$_2$Br(ClO_4). Although the behaviour of the magnetic properties of these complexes with temperature is simple, with θ small, they show a moment a good deal lower than that for the other cupric complexes reported here and in the literature (apart from Ray and Sen), at 1·7 B.M. No obvious reason for such a low value of the moment in a cupric complex is apparent from the theory;

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[14] Harris and Stevenson, unpublished work.
[15] Wells, *J.*, 1947, 1662.
[16] Figgis and Nyholm, *J.*, 1959, 331.

however, in the absence of evidence as to the actual stereochemistry it is not known whether any significance is to be attached to the result. To this information may be added the result [17] of $\mu_{\text{eff}} = 1{\cdot}9$ B.M. and $\theta = 0°$ for Cu(glycine)$_2$,H$_2$O.

The stereochemistry of the cupric ion in Cu(acetylacetone)$_2$ is known to be square planar from *X*-ray data.[18] Similarly, the nitrogen and chlorine atoms in Cu(dimethylglyoxime)Cl$_2$ are known to be coplanar. In the absence of *X*-ray information it seems reasonable to assign the square planar stereochemistry to Cu(*o*-phenanthroline)$_2$(ClO$_4$). Once again the moments are found to be about 1·9 B.M., and the dependence of the susceptibility on temperature close to the Curie law.

The only compound of essentially tetrahedral distribution of the ligands about the cupric ion available was Cs$_2$CuCl$_4$, which has been shown [19] to have a tetrahedron of chlorine atoms, around the cupric ion, slightly flattened so as to destroy the three-fold rotation axis but retain the four-fold rotation-reflection property (S_4 axis) of the tetrahedron. The moment of this compound is, indeed, a little higher than those of the other cupric compounds studied, at 2·0 B.M., but it is doubtful if much significance could be attached to the small difference. The magnetic behaviour conforms closely to Curie's law, with $\theta = 1°$. These results are not in good agreement with the properties expected for the cupric ion in a tetrahedral environment as outlined above, but could be understood if the departure from tetrahedral symmetry raised fairly large splittings of the ground-state d_ϵ levels, as is likely.

From these results and discussion it seems unlikely that the assignment of a tetrahedral stereochemistry to a number of cupric compounds made by Ray and Sen is justified. The magnetic properties of the cupric complexes studied have been found to be in accord with the presence of an octahedral or distorted octahedral arrangement (including square planar). The Curie law has been found to hold, even when the stereochemistry approximated to tetrahedral. It seems likely that many of the high values of θ reported by Ray and Sen are not real.

The curvature noticeable at high temperatures for most of the plots of Figs. 2—4 are due to the presence of a temperature-independent paramagnetism ($N\alpha$ term) of the same form as that reported [12] for K$_2$Cu(SO$_4$)$_2$,6H$_2$O and calculated [5] for CuSO$_4$,5H$_2$O, and also noticed in spin-paired cobaltous complexes.[16] The value of $N\alpha$ found was mostly around 60×10^{-6} in the molar susceptibility, *i.e.*, just the values previously reported and calculated. The $N\alpha$ term arises from second-order interactions through the magnetic field between the d_γ and d_ϵ levels, and is expected to remain substantially the same while either of the d_γ orbitals lies lowest—as in any form of octahedral or square planar stereochemistry. The magnitude of the effect when the d_ϵ orbitals lie lowest cannot be estimated without a detailed knowledge of the ground state and consequently it is not possible to comment on the absence of the effect in tetrahedral Cs$_2$CuCl$_4$. This is especially so because the effect is also inexplicably absent from CsCuCl$_3$, and from Cu(acetylacetone)$_2$.

EXPERIMENTAL

The measurements of the magnetic susceptibilities at various temperatures were made on the equipment described in Part I.[16]

The preparation and properties of the compounds Cu(*o*-phenanthroline)$_3$(ClO$_4$)$_2$, Cu(*o*-phenanthroline)$_2$Br(ClO$_4$), Cu(*o*-phenanthroline)$_2$Br$_2$, Cu(*o*-phenanthroline)$_2$(ClO$_4$)$_2$, and Cu(dipyridyl)$_3$(ClO$_4$)$_2$ will be published elsewhere by one of the authors (C. M. H.).

Cu(dimethylglyoxime)Cl$_2$ was prepared by mixing concentrated solutions of cupric chloride and dimethylglyoxime in equimolecular proportion in alcohol at the b. p. (Found: Cu, 25·3; Cl, 28·3. Calc. for CuC$_4$H$_8$O$_2$N$_2$Cl$_2$: Cu, 25·36; Cl, 28·50%).

CsCuCl$_3$ was prepared by evaporating to crystallisation an aqueous solution containing equimolecular proportions of CsCl and CuCl$_2$ (Found: Cu, 20·9. Calc. for CsCuCl$_3$: Cu = 20·98%).

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[17] Martin, unpublished work.

[18] Koyama, Saito, and Kuroya, *J. Inst. Polytechnic Osaka City Univ.*, 1953, **4**, 43.

[19] Helmholtz and Kruh, *J. Amer. Chem. Soc.*, 1952, **74**, 1176.

Cs_2CuCl_4 was prepared in the same way by employing a molar ratio of CsCl : $CuCl_2$ of 2 : 1 (Found: Cu, 13·4. Calc. for Cs_2CuCl_4: Cu, 13·47%).

The authors are indebted to Mrs. S. Djordjevic for the loan of the sample of Cu(acetylacetone)$_2$ (Found: Cu, 24·3; C, 45·73; H, 5·45. Calc. for $CuC_{10}H_{14}O_4$: Cu, 24·3; C, 45·9; H, 5·39%).

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