Contribution from the Chemistry Department,
Nagoya University, Chikusa, Nagoya, Japan

Magnetic Moments of Dichloro(1,2,4-triazole)copper(II) and Related Copper(II) Compounds

By MOTOMICHI INOUE, MICHIHIKO KISHITA, and MASAJI KUBO

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A variety of copper(II) complexes having nitrogen heterocycles as ligands have been prepared for the determination of the magnetic moments at room temperature. The majority of these compounds show subnormal magnetic moments except for $CuL^{II}X_2$ and $CuL^{I}X_2$ type complexes (L^{II} and L^{I}: bidentate and unidentate ligands, respectively) and those presumably having such units in crystals. The low magnetic moments suggest the existence of spin coupling through bidentate ligands. Dichloro(1,2,4-triazole)copper(II) bears a strong resemblance to copper(II) benzoate trihydrate; it shows a normal magnetic moment in spite of the existence in crystals of one-dimensional arrays of copper atoms linked by sharing the edges of coordination octahedra and also by bridging arrangements involving bidentate ligands.

Introduction

In a preceding paper,[1] we have reported that copper(II) benzoate trihydrate is the first known example of a crystalline copper(II) compound showing a normal magnetic moment at room temperature in spite of having a short Cu–Cu distance. Recently, Jarvis[2] has published the results of X-ray crystal analysis on dichloro(1,2,4-triazole)copper(II). The crystal structure of this compound is of particular interest because it bears a strong resemblance to that of copper(II) benzoate trihydrate as regards the complicated chain structure involving bidentate ligands. Therefore, we have undertaken to determine the magnetic moment of this compound along with those of other copper(II) compounds containing nitrogen heterocycles as ligands. In preparing various complexes, we have tried various methods of synthesis in order to obtain definite chemical species showing definite magnetic moments. This was done, because some copper(II) carboxylates have been reported to yield magnetically different crystal modifications.[1,3,4]

Experimental

Bis(1,2,4-triazolato)copper(II).—A modified Paolini–Goria method[5] was employed for the synthesis of this compound. An aqueous solution of 1,2,4-triazole (2 moles) was added to an ammoniacal solution of copper(II) sulfate (1 mole). Blue precipitates were formed and gradually turned violet. After standing for more than 2 hr., the precipitates were filtered off and washed with water. They were dissolved in about 6 *N* ammonia solution without warming. On standing, ammonia escaped and violet powder crystals were formed. *Anal.* Calcd. for $Cu(C_2H_2N_3)_2$: C, 24.1; H, 2.0; N, 42.1; Cu, 31.8. Found: C, 23.9; H, 2.3; N, 41.1; Cu, 31.2.

Dichloro(1,2,4-triazole)copper(II).—The Paolini–Goria method[5] was followed. Bis(1,2,4-triazolato)copper(II) was dissolved in about 4 *N* warm hydrochloric acid. On standing, emerald-green crystals were formed. *Anal.* Calcd. for $CuCl_2 \cdot (C_2H_3N_3)$: C, 11.8; H, 1.5; N, 20.6; Cu, 31.2. Found: C, 12.1; H, 1.5; N, 21.6; Cu, 31.1.

Chloro(1,2,4-triazolato)copper(II) Dihydrate.—The method of synthesis was the same as described by Paolini and Goria.[5] Dichloro(1,2,4-triazole)copper(II) was subjected to hydrolysis in warm water. Blue powder crystals were obtained. Alternatively, an aqueous solution of 1,2,4-triazole was added to a dilute solution of copper(II) chloride. *Anal.* Calcd. for $CuCl(C_2H_2N_3) \cdot 2H_2O$: C, 11.8; H, 3.0; N, 20.7; Cu, 31.3. Found: C, 12.4; H, 3.5; N, 21.0; Cu, 31.3.

Sulfatobis(1,2,4-triazole)copper(II) Trihydrate.—Bis(1,2,4-triazolato)copper(II) was dissolved in about 2% warm sulfuric acid. On standing in a refrigerator at about 6°, blue crystals separated. *Anal.* Calcd. for $CuSO_4 \cdot (C_2H_3N_3)_2 \cdot 3H_2O$: C, 13.7; H, 3.4; N, 23.9; Cu, 18.1; SO_4, 27.3; H_2O, 14.6. Found: C, 14.1; H, 3.1; N, 24.4; Cu, 17.6; SO_4, 26.6; H_2O, 13.5. We tried to prepare sulfatobis(1,2,4-triazole)copper(II) by the Paolini–Goria method.[5] However, samples obtained fluctuated in composition and magnetic data.

Chloro(benzotriazolato)copper(II).—When a dilute ethanol solution of copper(II) chloride (1 mole) was mixed with a concentrated ethanol solution of benzotriazole (1 mole), yellow-green precipitates were formed. They were thoroughly washed with ethanol. *Anal.* Calcd. for $CuCl(C_6H_4N_3)$: C, 33.2; H, 1.9; N, 19.4; Cu, 29.2. Found: C, 34.9; H, 2.1; N, 20.6; Cu, 29.1.

Bromo(benzotriazolato)copper(II).—A dilute ethanol solution of copper(II) bromide (1 mole) was added to an ethanol solution of benzotriazole (1 mole). Brownish green powder crystals formed and were thoroughly washed with ethanol. *Anal.* Calcd. for $CuBr(C_6H_4N_3)$: C, 27.6; H, 1.5; N, 16.1; Cu, 24.2. Found: C, 27.0; H, 2.6; N, 15.4; Cu, 23.8.

Dichloro(benzotriazole)copper(II).—When chloro(benzotriazolato)copper(II) was recrystallized from about 4 *N* hydrochloric acid, its hydrochloride was obtained as yellow-brown crystals. It readily decomposes in water. *Anal.* Calcd. for $CuCl_2 \cdot (C_6H_5N_3)$: C, 28.4; H, 2.1; N, 16.6; Cu, 25.1. Found: C, 28.6; H, 2.1; N, 16.6; Cu, 25.1.

Bis(imidazolato)copper(II).—This was synthesized by the method described by Brown and Aftergut.[6] The sample (blue modification) yielded X-ray powder patterns agreeing with those obtained by Brown and Aftergut as regards all major peaks.

Copper(II) sulfate pentahydrate (0.5 g.) was dissolved in a small amount of water and made up to about 25 ml. with ammonia solution, the final concentration of ammonia being about 4 *N*. An aqueous solution (about 15 ml.) of imidazole (0.25 g.) was added to the solution and left to stand. Precipitates which formed were filtered off. On standing, the filtrate separated dark green crystals (green modification). This compound turns dark brown and decomposes at about 240°. *Anal.* Calcd. for $Cu(C_3H_3N_2)_2$: C, 36.5; H, 3.1; N, 28.3; Cu, 32.1. Found: C, 36.7; H, 3.3; N, 28.0; Cu, 31.9.

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Ammonia solution was added to a solution (about 20 ml.) of copper(II) sulfate pentahydrate (0.5 g.) until the concentration of ammonia was 1–2 *N*. When an aqueous solution (10 ml.) of imidazole (0.25 g.) was added to the solution, green precipitates were immediately formed and gradually turned brown (brown modification). The precipitates were filtered off. On standing, the same compound separated from the filtrate. On heating above 200°, this compound turned dark brown and decomposed without melting. *Anal.* Calcd. for $Cu(C_3H_3N_2)_2$: C, 36.5; H, 3.1; N, 28.2; Cu, 32.1. Found: C, 36.5; H, 3.2; N, 28.2; Cu, 32.6.

The three crystal modifications yielded different X-ray powder patterns.

Bis(benzimidazolato)copper(II).—In accordance to Ghosh's method,[7] a solution of benzimidazole (0.3 g.) in warm water (80 ml.) was added to a solution (60 ml.) of copper(II) sulfate pentahydrate (0.3 g.). Green precipitates formed and gradually turned red. In order to complete the reaction, the solution was made weakly alkaline with a small amount of ammonia solution. After standing, the precipitates were filtered off and thoroughly washed with water. Alternatively, an ammoniacal solution of copper(II) sulfate was mixed with a weakly ammoniacal solution of benzimidazole to obtain the same red powder crystals. *Anal.* Calcd. for $Cu(C_7H_5N_2)_2$: C, 56.5; H, 3.4; N, 18.8; Cu, 21.3. Found: C, 56.1; H, 3.7; N, 18.4; Cu, 21.2.

Bis(pyrazolato)copper(II) Hemiammonia Hemihydrate.—An ammoniacal solution (10 ml.) of pyrazole (0.2 g.) was mixed with a solution (5 ml.) of copper(II) sulfate pentahydrate (0.5 g.), to which 6 *N* ammonia solution (about 25 ml.) was added in advance. Precipitates which formed were filtered off. On leaving the filtrate to stand, fine purple crystals separated. They were filtered off and washed with water. On heating at 110°, ammonia and water were liberated and the crystals turned brown. *Anal.* Calcd. for $Cu(C_3H_3N_2)_2 \cdot 0.5NH_3 \cdot 0.5H_2O$: C, 33.5; H, 4.0; N, 29.5; Cu, 29.5; $0.5NH_3 + 0.5H_2O$, 8.1. Found: C, 33.8; H, 4.3; N, 30.1; Cu, 29.1; $0.5NH_3 + 0.5H_2O$, 8.3.

Dichlorobis(3,5-dimethylpyrazole)copper(II).—A dilute ethanol solution of copper(II) chloride (1 mole) was added to an ethanol solution of 3,5-dimethylpyrazole (2 moles). Yellow-green precipitates formed immediately. Water could be used as a solvent in place of ethanol. Recrystallization from benzene yielded yellow-green crystals. *Anal.* Calcd. for $CuCl_2 \cdot (C_5H_8N_2)_2$: C, 36.8; H, 4.9; N, 17.2; Cu, 19.4; Cl, 21.7. Found: C, 36.6; H, 5.2; N, 16.7; Cu, 19.4; Cl, 21.7.

Sulfatobis(3,5-dimethylpyrazole)copper(II) Dihydrate.—A concentrated aqueous solution of 3,5-dimethylpyrazole (2 moles) was added to a dilute solution of copper(II) sulfate (1 mole). On standing, blue needle crystals separated. Crystals differing in habit could be obtained depending on the mole ratio of copper(II) sulfate and 3,5-dimethylpyrazole as well as on the concentration of solutions. However, they gave identical X-ray powder patterns. The compound did not give a constant weight decrease on heating at 100°, probably because of the partial loss of the ligand molecules. *Anal.* Calcd. for $CuSO_4 \cdot (C_5H_8N_2)_2 \cdot 2H_2O$: C, 31.5; H, 6.1; N, 13.5; Cu, 16.1. Found: C, 31.0; H, 5.2; N, 14.4; Cu, 16.4.

Dinitratotetrakis(3,5-dimethylpyrazole)copper(II).—Copper(II) nitrate trihydrate (0.5 g.) and 3,5-dimethylpyrazole (0.4 g.) were dissolved in water (about 40 ml.). On standing, deep blue crystals separated. *Anal.* Calcd. for $Cu(NO_3)_2 \cdot (C_5H_8N_2)_4$: C, 42.0; H, 5.7; N, 24.5; Cu, 11.1. Found: C, 41.1; H, 5.5; N, 23.5; Cu, 10.9. This compound decomposes on heating at about 100°, leading to a considerable loss in weight.

Diacetatobis(3,5-dimethylpyrazole)copper(II).—A concentrated aqueous solution of 3,5-dimethylpyrazole (2 moles) was added to a concentrated solution of copper(II) acetate (1 mole). The mixture was acidified with a small amount of acetic acid and slowly concentrated over a water bath. Blue needle crystals were obtained and they were recrystallized from water acidified with a small amount of acetic acid. *Anal.* Calcd. for $Cu(CH_3CO_2)_2 \cdot (C_5H_8N_2)_2$: C, 45.0; H, 6.0; N, 15.0; Cu, 17.0. Found: C, 45.0; H, 5.9; N, 14.7; Cu, 17.0.

Diacetato(3,5-dimethylpyrazole)copper(II).—Copper(II) acetate monohydrate (1 mole) and 3,5-dimethylpyrazole (1 mole) were dissolved in a minimum amount of warm ethanol. When the solution was left to stand in a refrigerator at about 6°, green crystals separated. *Anal.* Calcd. for $Cu(CH_3CO_2)_2 \cdot (C_5H_8N_2)$: C, 38.9; H, 5.1; N, 10.1; Cu, 22.9. Found: C, 38.3; H, 4.9; N, 9.4; Cu, 23.1.

Magnetic Measurements and Results

The magnetic susceptibility was determined at room temperature[1,8] by means of a Gouy magnetic apparatus provided with a semimicrobalance and an electromagnet capable of yielding a field of about 23,000 oersteds with 10-mm. separation between pole pieces. From the observed susceptibilities, the magnetic moments per copper atom were evaluated. The diamagnetic correction was made on the basis of observed magnetic susceptibilities of ligands (1,2,4-triazole, -38×10^{-6} e.m.u.; benzotriazole, -81×10^{-6} e.m.u.; benzimidazole, -76×10^{-6} e.m.u.; 3,5-dimethylpyrazole, -56×10^{-6} e.m.u.[9]) and data reported in the literature[10] for other constituents. The results are shown in Table I.

TABLE I

MAGNETIC SUSCEPTIBILITIES PER GRAM (C.G.S., E.M.U.) AND MAGNETIC MOMENTS (BOHR MAGNETONS) OF DICHLORO(1,2,4-TRIAZOLE)COPPER(II) AND RELATED COPPER(II) COMPOUNDS

Compounds[a]		Temp., °C.	$\chi_g \times 10^6$	μ, B.M.[b]
$Cu(Tr)_2$		20	5.50	1.66
$CuCl_2(TrH)$		20	6.45	1.81
$CuCl(Tr) \cdot 2H_2O$		20	3.20	1.32
$CuSO_4(TrH)_2 \cdot 3H_2O$		20	2.58	1.55
$CuCl(Bt)$		26	4.62	1.63
$CuBr(Bt)$		26	2.81	1.43
$CuCl_2(BtH)$		26	5.06	1.84
$Cu(Im)_2$	blue	20	5.00	1.57
	green	30	5.14	1.62
	brown	30	4.10	1.46
$Cu(Bm)_2$		30	3.67	1.74[c]
$Cu(Py)_2 \cdot 0.5NH_3 \cdot 0.5H_2O$		30	3.90	1.49
$CuCl_2(DpH)_2$		17	3.90	1.83
$CuSO_4(DpH)_2 \cdot 2H_2O$		17	3.20	1.81
$Cu(NO_3)_2(DpH)_4$		17	1.98	1.80
$Cu(CH_3CO_2)_2(DpH)_2$		17	3.65	1.89
$Cu(CH_3CO_2)_2(DpH)$		17	2.65	1.41

[a] TrH, 1,2,4-triazole; BtH, benzotriazole; ImH, imidazole; BmH, benzimidazole; PyH, pyrazole; DpH, 3,5-dimethylpyrazole. [b] The moments are calculated for the particular temperature listed and are not expected to be constant, especially for the compounds showing a subnormal magnetic moment. [c] 1.81 B.M. at 32°.[7]

Discussion

Normal magnetic moments have been observed for dichloro(1,2,4-triazole)copper(II), dichloro(benzotriazole)copper(II), and some copper(II) complexes con-

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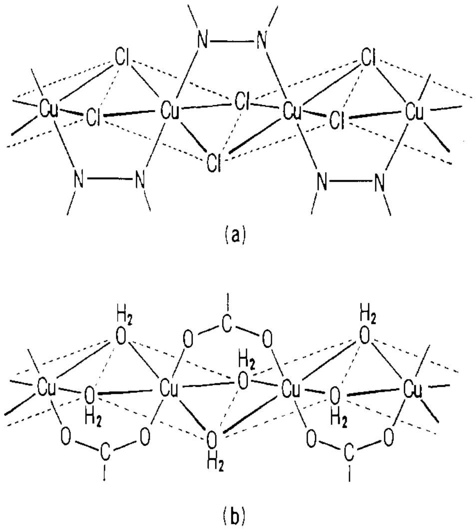

Figure 1.—Linear chains in the crystals of (a) dichloro(1,2,4-triazole)copper(II) and (b) copper(II) benzoate trihydrate.

taining 3,5-dimethylpyrazole, whereas all other compounds studied show subnormal magnetic moments, *i.e.*, moments smaller than the spin moment, 1.73 B.M., for one unpaired electron. A 3,5-dimethylpyrazole molecule acts as a unidentate ligand, because one of the two nitrogen atoms in the molecule has a hydrogen atom attached to it and hence has no lone pair of electrons. All other nitrogen-containing heterocyclic molecules and groups involved in copper(II) compounds studied have, in a molecule, at least two basic nitrogen atoms and hence can behave as bidentate ligands. For steric reasons, each bidentate ligand occupies coordination sites belonging to different copper atoms. This has been confirmed by an X-ray investigation on dichloro(1,2,4-triazole)copper(II).[2] Subnormal magnetic moments observed for the majority of copper(II) compounds involving the bidentate ligands indicate that spin interaction between copper(II) ions is appreciable through some bonds in nitrogen heterocycles.

It is rather surprising to find that spin interaction is apparently absent in dichloro(1,2,4-triazole)copper(II) and dichloro(benzotriazole)copper(II) in spite of the existence of bridging arrangements between copper atoms. In fact, X-ray analysis carried out by Jarvis[2] has shown that in the crystals of dichloro(1,2,4-triazole)copper(II), each copper atom has a distorted octahedral coordination group consisting of four chlorine and two nitrogen atoms and that the structural unit is an infinite chain in which octahedral groups are joined by sharing edges and are also linked by 1,2,4-triazole molecules with Cu–Cu separation equal to 3.40 Å. The chain structure is illustrated schematically in Figure 1a. It is interesting to note the close analogy of this structure to that of copper(II) benzoate trihydrate, which also shows a normal magnetic moment (1.87 B.M.[1]). X-Ray crystal analysis carried out by Koizumi, *et al.*,[11] has shown that in this crystal neighboring copper atoms are 3.15 Å. from each other and are bridged by two oxygen atoms and one Cu–O–C–O–Cu link to form linear chains $[Cu\cdot C_6H_5CO_2\cdot 2H_2O]_n$ shown in Figure 1b with $[H_2O\cdot C_6H_5CO_2]_n$ intervening between them. Evidently, copper(II) complexes of the general formula $CuL^{II}X_2$ (L^{II}, a bidentate ligand; X, a halogen atom or a water molecule) are capable of forming a chain structure of this type under favorable condition. Presumably, the formation of a one-dimensional array of copper atoms rather than separate Cu–Cu pairs as in copper(II) acetate monohydrate[12] or acetylacetonemono(*o*-hydroxyanil)copper(II)[13,14] is responsible for the apparently complete absence of spin interaction between copper atoms.

Except for diacetato(3,5-dimethylpyrazole)copper(II), all 3,5-dimethylpyrazole complexes studied show normal magnetic moments of 1.80–1.89 B.M. Since they have, per copper atom, at least four atoms, groups, water molecules, or unidentate ligand molecules capable of being coordinated on a copper atom, structures are conceivable in which no bridging arrangements exist between copper atoms, as in the crystals of dichlorobis(pyridine)copper(II) studied by Dunitz.[15] Diacetato(3,5-dimethylpyrazole)copper(II), having only three coordinating groups in its monomeric formula, cannot complete the square coordination of copper, unless dimeric molecules or higher aggregates are formed. The observed subnormal magnetic moment, 1.41 B.M., suggests possible formation of binuclear complex structure similar to that in diacetato(pyridine)copper(II).[16]

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