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Low Magnetic Moments and the Structure of Urea Complexes of Copper(II) *n*-Alkanoates

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A variety of addition compounds of copper(II) *n*-alkanoates with urea have been prepared and the magnetic moments have been determined. Monourea compounds are formed preferentially for lower members up to copper(II) butyrate while hemiurea derivatives are obtainable for copper(II) pentanoate and higher homologs. It is concluded from the observed subnormal magnetic moments 1.40 ± 0.03 B.M. that the structure of the monourea compounds is analogous to that of copper(II) acetate monohydrate. The hemiurea compounds also have binuclear structural units involving a pair of copper atoms. The magnetic moment of 1.67 B.M. of copper(II) formate bisurea dihydrate is close to the spin moment 1.73 B.M. for one unpaired electron and is almost identical with that of copper(II) formate tetrahydrate.

Introduction

The binuclear structure of copper(II) acetate monohydrate has been established by X-ray crystal analysis carried out by van Niekerk and Schoening.[1] A characteristic feature of the structure involves copper atoms bridged in pairs by four acetate groups with two water molecules occupying the terminal positions. The decrease in magnetic moment of this compound with decreasing temperature as observed by Figgis and Martin[2] indicates the presence of spin interaction between two copper atoms in a pair. The observed moments 1.39 and 1.40 B.M.[2] for copper(II) acetate and its monohydrate, respectively, at room temperature are subnormal, *i.e.*, considerably smaller than the spin moment 1.73 B.M. for one unpaired electron. Accordingly, from subnormal magnetic moments observed for copper(II) carboxylates and their derivatives, one can infer the existence of paired copper atoms in crystals. We have determined the magnetic moments of a number of urea complexes of copper(II) *n*-alkanoates to see whether or not binuclear structure involving copper atoms exists in the crystals of these complexes.

Preparation of Materials

Copper(II) Formate Bisurea Dihydrate.—A mixture of saturated copper(II) formate solution (1 mole) and saturated urea solution (3 moles) was slowly concentrated over a water bath below 60°. When the solution became turbid, it was quickly filtered while still warm. On standing in air, the filtrate separated pale blue crystals, which were recrystallized from a minimum amount of warm water at about 60°. (In order to eliminate the effect of atmospheric carbon dioxide, a small amount of formic acid was added to the solution for recrystallization.) The aqueous solution is blue, while the methanol solution is green (see below).

Anal. Calcd. for $Cu(HCO_2)_2 \cdot 2(NH_2)_2CO \cdot 2H_2O$: C, 15.5; H, 4.6; N, 18.1; Cu, 20.5. Found: C, 15.8; H, 4.9; N, 18.0; Cu, 21.0.

Copper(II) Formate Monourea.—The foregoing compound was dissolved in a minimum amount of methanol. The solution was concentrated at room temperature under reduced pressure. Fine green crystals separated, which were recrystallized from methanol and washed with ether. Alternatively, copper(II) carbonate was added to a solution of urea in formic acid to obtain a crude sample of this compound. The compound gradually decomposes before it melts at about 160°. It is soluble in water and methanol, yielding blue and green solutions, respectively.

Anal. Calcd. for $Cu(HCO_2)_2 \cdot (NH_2)_2CO$: C, 16.9; H, 2.8; N, 13.1; Cu, 29.8. Found: C, 17.1; H, 3.0; N, 13.2; Cu, 30.3.

Copper(II) Acetate Monourea Monohydrate.—A saturated solution of copper(II) acetate (1 mole) was mixed with a saturated solution of urea (2 moles or more). The subsequent treatment was the same as for copper(II) formate bisurea dihydrate. The compound forms green crystals soluble in water, methanol, and ethanol.

Anal. Calcd. for $Cu(CH_3CO_2)_2 \cdot (NH_2)_2CO \cdot H_2O$: C, 23.1; H, 4.7; N, 10.8; Cu, 24.5. Found: C, 23.4; H, 4.6; N, 11.1; Cu, 24.4.

Copper(II) Acetate Monourea.—An ethanol solution of urea (about 2 moles) was added to an ethanol solution of copper(II) acetate monohydrate (1 mole). The yellow-green precipitate which formed was recrystallized from ethanol and washed with ether. The compound is soluble in water, methanol, and ethanol. It gradually decomposes at about 120°.

Anal. Calcd. for $Cu(CH_3CO_2)_2 \cdot (NH_2)_2CO$: C, 24.9; H, 4.2; N, 11.6; Cu, 26.3. Found: C, 24.3; H, 4.6; N, 11.6; Cu, 25.8.

Copper(II) Propionate Monourea.—A concentrated solution of copper(II) propionate in ethanol was mixed with a saturated solution of urea in ethanol in mole ratio equal to about 1:3. On standing, yellow-green crystals separated which were recrystallized from ethanol. Water can also be used as a solvent.

Anal. Calcd. for $Cu(C_2H_5CO_2)_2 \cdot (NH_2)_2CO$: C, 31.2; H, 5.2; N, 10.4; Cu, 23.5. Found: C, 32.0; H, 5.5; N, 10.1; Cu, 23.2.

Copper(II) *n*-Butyrate Monourea.—This compound was synthesized in the same manner as the foregoing one. However, the use of water as a solvent is disadvantageous because the solubility of the copper salt is small.

Anal. Calcd. for $Cu(C_3H_7CO_2)_2 \cdot (NH_2)_2CO$: C, 36.3; H, 6.1; N, 9.5; Cu, 21.3. Found: C, 36.9; H, 6.3; N, 9.2; Cu, 21.4.

Copper(II) *n*-Pentanoate Hemiurea.—A saturated solution of copper(II) *n*-pentanoate in ethanol was saturated with urea. On standing in a refrigerator at about 6°, blue-green crystals separated. They were recrystallized from ethanol.

Anal. Calcd. for $Cu(C_4H_9CO_2)_2 \cdot 0.5(NH_2)_2CO$: C, 42.7; H, 6.8; N, 4.8; Cu, 21.4. Found: C, 43.0; H, 6.9; N, 5.0; Cu, 21.0.

Copper(II) *n*-Hexanoate Hemiurea.—Urea was added to a saturated solution of copper(II) *n*-hexanoate in ethanol. On standing at room temperature, fine blue-green crystals separated and were purified by recrystallization from ethanol.

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[1] J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 227 (1953).

[2] B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956).

Table I

Magnetic Susceptibilities per Gram (c.g.s., e.m.u.) and Magnetic Moments (Bohr Magnetons) of the Urea Complexes of Copper(II) *n*-Alkanoates at Room Temperature[a]

Compounds	$\chi_g \times 10^6$	μ_{eff}
Cu(II) formate bisurea dihydrate	3.46	1.67
Cu(II) formate monourea	2.01	1.08
Cu(II) acetate monourea monohydrate	2.79	1.39
Cu(II) acetate monourea	2.96	1.37
Cu(II) propionate monourea	2.61	1.39
Cu(II) butyrate monourea	2.43	1.42
Cu(II) pentanoate hemiurea	2.44	1.43
Cu(II) hexanoate hemiurea	2.05	1.40
Cu(II) hexanoate monourea	1.81	1.39
Cu(II) heptanoate hemiurea	1.89	1.42
Cu(II) octanoate hemiurea	1.69	1.42
Cu(II) nonanoate hemiurea	1.42	1.39
Cu(II) decanoate hemiurea	1.39	1.43

[a] 17° for the derivatives of copper(II) formate and acetate; 18° for others.

Anal. Calcd. for $Cu(C_5H_{11}CO_2)_2 \cdot 0.5(NH_2)_2CO$: C, 46.4; H, 7.5; N, 4.4; Cu, 19.6. Found: C, 46.4; H, 7.6; N, 4.4; Cu, 19.6.

Copper(II) *n*-Hexanoate Monourea.—A large amount (about three times the equivalent amount) of urea was dissolved in a concentrated solution of copper(II) *n*-hexanoate in methanol. On leaving the mixture in a refrigerator at about 6°, yellow-green crystals were formed. Since this compound is less stable than the hemiurea derivative, the crystals were quickly separated from the mother liquor by suction followed by washing with ether. In order to prevent atmospheric moisture from condensing on the crystals, they were promptly warmed to a temperature slightly higher than room temperature.

Anal. Calcd. for $Cu(C_5H_{11}CO_2)_2 \cdot (NH_2)_2CO$: C, 44.2; H, 7.4; N, 8.0; Cu, 17.9. Found: C, 44.5; H, 7.6; N, 7.7; Cu, 17.3.

Copper(II) *n*-Heptanoate Hemiurea.—This and the following compounds were prepared in the same way as for copper(II) hexanoate hemiurea. They form fine blue-green crystals.

Anal. Calcd. for $Cu(C_6H_{13}CO_2)_2 \cdot 0.5(NH_2)_2CO$: C, 49.5; H, 8.0; N, 4.0; Cu, 18.1. Found: C, 48.7; H, 7.9; N, 4.0; Cu, 17.9.

Copper(II) *n*-Octanoate Hemiurea.—*Anal.* Calcd. for $Cu(C_7H_{15}CO_2)_2 \cdot 0.5(NH_2)_2CO$: C, 52.2; H, 8.5; N, 3.7; Cu, 16.7. Found: C, 52.2; H, 8.5; N, 3.7; Cu, 16.7.

Copper(II) *n*-Nonanoate Hemiurea.—*Anal.* Calcd. for $Cu(C_8H_{17}CO_2)_2 \cdot 0.5(NH_2)_2CO$: C, 54.5; H, 8.9; N, 3.5; Cu, 15.6. Found: C, 54.6; H, 8.9; N, 3.6; Cu, 15.7.

Copper(II) *n*-Decanoate Hemiurea. *Anal.* Calcd. for $Cu(C_9H_{19}CO_2)_2 \cdot 0.5(NH_2)_2CO$: C, 56.4; H, 9.3; N, 3.2; Cu, 14.6. Found: C, 56.5; H, 9.2; N, 3.5; Cu, 14.3.

Magnetic Measurements and Results

Magnetic susceptibility was determined at room temperature[3] 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 were evaluated per copper atom. The diamagnetic contribution of ligands was calculated from the observed susceptibilities of the corresponding acids, urea, and water. Utmost precaution was taken to avoid possible contamination of ferromagnetic impurities in samples. It was confirmed that the observed values were not altered by repeated recrystallization. The results are shown in Table I.

Discussion

The most general types of the urea complexes of copper(II) *n*-alkanoates are monourea and hemiurea derivatives. The monourea compounds are formed preferentially for lower members up to copper(II) butyrate, while hemiurea derivatives are obtainable for copper(II) pentanoate and higher homologs. It is interesting to note that copper(II) *n*-alkanoates obtainable in the hydrated state (copper(II) formate tetrahydrate, copper(II) acetate monohydrate, copper(II) propionate monohydrate, and copper(II) butyrate monohydrate are known) form monourea compounds, whereas those existing only in the anhydrous state give rise to hemiurea complexes. This suggests that urea adds more readily to copper(II) alkanoates than water does.

It is very likely that copper(II) butyrate hemiurea and copper(II) pentanoate monourea also exist, although we have not succeeded in obtaining them in a pure state. However, we could prepare copper(II) hexanoate monourea, which was less stable than the corresponding hemiurea derivative. The urea complexes of copper(II) formate and acetate are obtainable in the hydrated state also. It is probable that some higher homologs beyond copper(II) decanoate form urea complexes. However, with increasing number of carbon atoms in carboxylic acids, the solubility of copper(II) *n*-alkanoates and their urea derivatives in water and in ethanol decreases, rendering preparation and purification more difficult.

Dioxane, pyridine, and picoline isomers are known to form addition compounds with copper(II) formate and acetate.[4] A preliminary report has been published on the pyridine derivative of copper(II) propionate. Mention should be made here that copper(II) *n*-alkanoates beyond the propionate have not been reported to form hydrates and addition compounds of this sort.

The observed moment 1.67 B.M. of copper(II) formate bisurea dihydrate[5] is practically identical with that of copper(II) formate tetrahydrate 1.67 (1.70,[6] 1.67[7]) B.M. Kiriyama, *et al.*,[8] have carried out a complete X-ray crystal analysis on copper(II) formate tetrahydrate. It was found that the oxygen atoms of two water molecules are 2.36 Å. distant from a copper atom to complete a distorted octahedron with four closer oxygen atoms (Cu–O distance, 2.00–2.01 Å.) belonging to formate groups, while the same number of water molecules are not linked to any copper atoms but are hydrogen bonded to other oxygen atoms. The

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[3] M. Kondo, M. Kishita, M. Kimura, and M. Kubo, *Bull. Chem. Soc. Japan*, **29**, 305 (1956); M. Kishita, Y. Muto, and M. Kubo, *Australian J. Chem.*, **10**, 386 (1957); M. Kondo and M. Kubo, *J. Phys. Chem.*, **61**, 1648 (1957).

[4] R. L. Martin and H. Waterman, *J. Chem. Soc.*, 2960 (1959).

[5] M. Kishita and M. Kubo, *Naturwissenschaften*, **49**, 230 (1962).

[6] J. Amiel, *Compt. rend.*, **207**, 1097 (1938).

[7] R. L. Martin and H. Waterman, *J. Chem. Soc.*, 1359 (1959).

[8] R. Kiriyama, H. Ibamoto, and K. Matsuo, *Acta Cryst.*, **7**, 482 (1954).

agreement of magnetic moments of the two complexes and the existence of crystallographically nonequivalent water molecules in the tetrahydrate along with the close similarity in color and cleavage between these complexes suggest that two molecules of water in the tetrahydrate can be replaced with two urea molecules to form the bisurea dihydrate without affecting appreciably the two-dimensional network structure involving copper atoms.

Copper(II) formate monourea shows a subnormal magnetic moment of 1.08 B.M., indicating the presence of paired copper atoms as in the crystals of copper(II) acetate monohydrate.[1] It is presumed that in this binuclear complex, copper atoms are bridged in pairs by four formate groups with two urea molecules occupying the terminal positions. This is interesting because unlike other copper(II) carboxylates,[9] copper(II) formate and its stable derivatives are known to show moments[7,10] close to the theoretical spin-only moment of 1.73 B.M. for one unpaired electron except in dioxane solution.[4,11]

All the urea complexes of copper(II) acetate and higher homologs studied show typically subnormal magnetic moments equal to 1.40 ± 0.03 B.M. The values are close to the moments of anhydrous copper(II) *n*-alkanoates and hydrated ones.[2,6,9] Undoubtedly, urea molecules in the monourea complexes occupy the same positions about copper atoms as do water molecules in the crystals of copper(II) acetate monohydrate. In fact, it has been found by X-ray crystal analysis[12] that pyridine can replace water in the latter compound without affecting the characteristic binuclear structure involving copper atoms. Probably, oxygen atoms rather than nitrogen atoms of urea molecules are directly coordinated on copper atoms.[13]

The observed subnormal magnetic moments of copper(II) *n*-alkanoate hemiureas indicate the presence of paired copper atoms in crystals. It is unlikely that $Cu_2(C_nH_{2n+1}CO_2)_2\cdot(NH_2)_2CO$ is the structural unit composing the crystals, because it is not probable that copper atoms have vacant coordination sites, whereas oxygen and nitrogen atoms of urea exist in the crystals without participating in coordination.

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[9] R. L. Martin and H. Waterman, *J. Chem. Soc.*, 2545 (1957); M. Kondo and M. Kubo, *J. Phys. Chem.*, **62**, 1558 (1958); O. Asai, M. Kishita, and M. Kubo, *ibid.*, **63**, 96 (1959).

[10] G. A. Barclay and C. H. L. Kennard, *J. Chem. Soc.*, 3289 (1961).

[11] R. L. Martin and A. Whitley, *ibid.*, 1394 (1958).

[12] G. A. Barclay and C. H. L. Kennard, *ibid.*, 5244 (1961).

[13] R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **79**, 1575 (1957).

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Magnetic Moments of Copper(II) Salicylate, Copper(II) Benzoate, and Some Related Compounds

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Copper(II) salicylate tetrahydrate and anhydrous copper(II) salicylate can be obtained in two different crystal modifications, in one of which the magnetic moment per copper atom is normal whereas in the other it is subnormal. Copper(II) benzoate trihydrate shows a normal magnetic moment in spite of the close distance of approach and bridging arrangement of copper atoms in crystals. Anhydrous copper(II) benzoate forms three different modifications, each characterized by its color, magnetic moment, and X-ray powder patterns. The addition compounds of copper(II) benzoate with benzoic acid, ethanol, and urea show subnormal magnetic moments characteristic of some crystalline copper(II) carboxylates having the binuclear structure of copper atoms.

Introduction

On the basis of their magnetic moments at room temperature, copper(II) compounds can be classified into two main groups. A great majority of these compounds show normal moments (1.8–2.0 Bohr magnetons), indicating the absence of any appreciable spin coupling between unpaired electrons belonging to copper atoms. On the other hand, a number of copper(II) compounds have been reported to show moments considerably smaller than the spin moment 1.73 B.M. for one unpaired electron (subnormal moments approximately equal to 1.4 B.M. or less). Some copper(II) carboxylates[1,2] and the so-called tricoordinated copper(II) complexes[3] belong to this category. Obviously, some kind of spin interaction either of a direct nature or of a super-exchange type must be responsible for the subnormal moments. In fact, it has been shown by X-ray crystal analysis that in copper(II) acetate monohydrate,[4] copper atoms are bridged in pairs by four acetate groups to form dimer molecules in which the Cu–Cu

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[1] B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956); R. L. Martin and H. Waterman, *ibid.*, 2545 (1957); R. L. Martin and A. Whitley, *ibid.*, 1394 (1958); R. L. Martin and H. Waterman, *ibid.*, 1359, 2960 (1959).

[2] M. Kondo and M. Kubo, *J. Phys. Chem.*, **62**, 468, 1558 (1958); O. Asai, M. Kishita, and M. Kubo, *ibid.*, **63**, 96 (1959); M. Inoue, M. Kishita, and M. Kubo, *Acta Cryst.*, **16**, 699 (1963); M. Kishita, M. Inoue, and M. Kubo, *Inorg. Chem.*, **3**, 237 (1964).

[3] M. Kishita, Y. Muto, and M. Kubo, *Australian J. Chem.*, **10**, 386 (1957), **11**, 309 (1958); M. Kubo, Y. Kuroda, M. Kishita, and Y. Muto, *ibid.*, **16**, 7 (1963).

[4] J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 227 (1953).