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# Infrared Spectra of Urea Complexes of Copper(II) *n*-Alkanoates

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The infrared absorption spectra of various urea complexes of copper(II) carboxylates were recorded and the assignments of observed frequencies have been carried out to various modes of vibration. On the basis of comparison of the observed spectra with those of related compounds, it is concluded that copper(II) carboxylate monoureas and hemiureas form dimer molecules in crystals as in copper(II) acetate monohydrate, that copper(II) formate bisurea dihydrate has a crystal structure bearing resemblance to that of copper(II) formate tetrahydrate, and that urea molecules in these urea complexes are involved in bonding by electrostatic forces or hydrogen bondings instead of being bonded to copper atoms by coordination bonds.

Urea forms various addition compounds with copper(II) *n*-alkanoates.[1,2] The most general types of the urea complexes are copper(II) *n*-alkanoate monoureas, $Cu(C_nH_{2n+1}CO_2)_2\cdot(NH_2)_2CO$ ($n$=0—3, 5), and copper(II) *n*-alkanoate hemiureas, $Cu(C_nH_{2n+1}CO_2)_2\cdot 0.5(NH_2)_2CO$ ($n$=4—9). In addition, the hydrated urea complexes of copper(II) formate and acetate, $Cu(HCO_2)_2\cdot 2(NH_2)_2CO\cdot 2H_2O$ and $Cu(CH_3CO_2)_2\cdot(NH_2)_2CO\cdot H_2O$, can be prepared in the crystalline state. We have observed the magnetic moments of these copper(II) compounds and found that except for copper(II) formate bisurea dihydrate, they show subnormal magnetic moments, 1.40±0.03 Bohr magnetons, per copper atom at room temperature, suggesting the existence of paired copper atoms in crystals. 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.[3] However, the structures of the hemiurea complexes and the hydrated urea complexes are open to speculation so long as the magnetic data alone are taken into account. The present investigation has been undertaken in order to gain some information from infrared spectroscopy about the role of urea molecules possibly participating in coordination on copper atoms.

## Experimental

Materials tested were prepared by methods described in a previous paper.[2] Infrared absorptions were recorded over a wave number range from 4000 to 200 cm$^{-1}$ using a Model DS-402G grating infrared spectrophotometer from Japan Spectroscopic Company. In the frequency range above 400 cm$^{-1}$, all samples were run as potassium bromide disks and checked in Nujol mulls. Below 430 cm$^{-1}$, spectra were obtained using Nujol mulls. Potassium bromide plates and thin polyethylene films were used as cell windows for Nujol mulls in the two regions, respectively.

## Results

**Copper(II) Acetate Monourea.**—The absorptions of copper(II) acetate monourea are compared

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

[2] M. Kishita, M. Inoue and M. Kubo, *Inorg. Chem.*, **3**, 237 (1964).

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

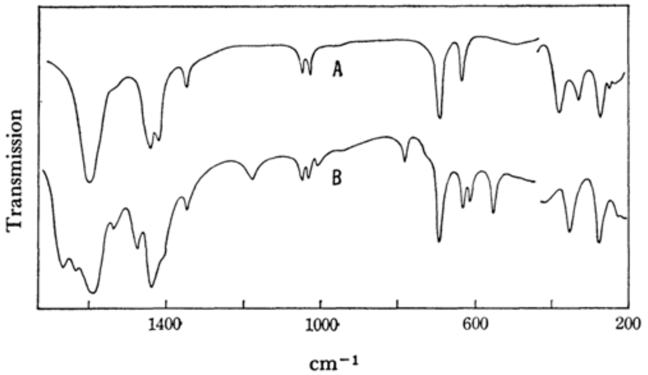

Fig. 1. Infrared spectra of (A) copper(II) acetate monohydrate and (B) copper(II) acetate monourea.

TABLE I. INFRARED ABSORPTIONS (cm$^{-1}$) OF COPPER(II) ACETATE, COPPER(II) ACETATE MONOHYDRATE, AND COPPER(II) ACETATE MONOUREA*

| Copper(II) acetate | Copper(II) acetate monohydrate | Copper(II) acetate monourea |
|---|---|---|
| | | 1670 s |
| | | 1635 sh |
| 1590 vs | 1602 vs | 1595 vs |
| hump | hump | 1535m |
| | | 1475 s |
| 1441 vs | 1441 vs | 1440 vs |
| 1412 vs | 1418 vs | 1415 sh |
| 1352m | 1351m | 1355m |
| | | 1178m |
| 1051m | 1051m | 1050m |
| 1038 sh | 1032m | 1032m |
| | | 1006m |
| 945w | hump | hump |
| | | 782m |
| | | 725w |
| 692 s | 690 s | 687 s |
| 625m | 629m | 627m |
| | | 614m |
| | | 550m |
| 382m | 375m | |
| 340m | 330w | 350m |
| 284m | 274m | 274m |
| | 254w | |
| ~240w | ~235w | ~233w |

* vs, very strong. s, strong. m, medium. w, weak. sh, shoulder.

TABLE II. INFRARED ABSORPTIONS (cm$^{-1}$) OF COPPER(II) CAPROATE, COPPER(II) CAPROATE MONOUREA, AND COPPER(II) CAPROATE HEMIUREA*

| Copper(II) caproate | Copper(II) caproate monourea | Copper(II) caproate hemiurea |
|---|---|---|
| | 1675 s | 1675 s |
| | 1655 s | 1660 s |
| | 1625 s | 1626 s |
| | | 1614 s |
| 1585 vs | 1585 vs | 1586 vs |
| 1510m | 1535m | 1535m |
| 1432m | 1465 s | 1460 s |
| 1416 s | 1430 s | 1427 s |
| 1378—1191 p | 1380—1230 p | 1380—1194 p |
| | 1170m | 1175 sh |
| 1113w | 1114m | 1115m |
| | 1000w | |
| 895w | 890w | 892w |
| 848w | 850w | 853w |
| | 778 sh | |
| | 772m | 778w |
| | 737m | 740 sh |
| 725m | 722 sh | 720m |
| 664m | 651m | 670m |
| | | 645w |
| | 605m | 599m |
| | 541m | 532m |
| | 443m | |
| 385m | 389m | 400m |
| 342w | 334m | 352m |
| 303w | | |
| 245m | 260m | 270m |

* p, band progression.

with those of copper(II) acetate and copper(II) acetate monohydrate⁴⁾ in Table I. In the wave number range 1800—400 cm$^{-1}$, all absorption peaks characteristic of anhydrous copper(II) acetate, which shows practically the same spectrum as that of copper(II) acetate monohydrate in this frequency range, appear in the spectrum of copper(II) acetate monourea without any appreciable change in the position, the intensity, and the shape of absorption bands as shown in Fig. 1. Accordingly, additional absorptions appearing in the spectrum of copper(II) acetate monourea can be assigned to vibrations involving urea molecules. On the other hand, no such clear correspondence can be made below

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4) Y. Kuroda. *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **82**, 1624 (1961).

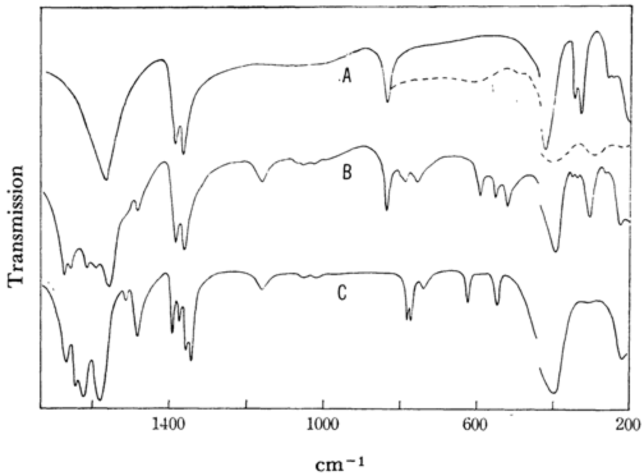

Fig. 2. Infrared spectra of (A) anhydrous copper(II) formate (full curve), copper(II) formate tetrahydrate (broken curve), (B) copper(II) formate bisurea dihydrate, and (C) copper(II) formate monourea.

400 cm$^{-1}$, probably because lattice vibrations, librations, etc. are involved in the spectra. In a region beyond 1800 cm$^{-1}$, only NH stretching vibrations are observable as intense bands.

Other copper(II) *n*-alkanoate monoureas were tested and yielded analogous results.

**Copper(II) Caproate (*n*-Hexanoate) Hemiurea.**—Table II shows the absorptions of copper(II) caproate, copper(II) caproate monourea, and copper(II) caproate hemiurea. In the region of band progressions (about 1350—1200 cm$^{-1}$), the spectra are complicated and no definite correspondence of absorption peaks can be found between the spectra of these compounds, presumably owing to difference in the interactions of methylene chains in crystals. However, major peaks of copper(II) caproate appearing in the wave number range 1800—400 cm$^{-1}$ can be found in the spectra of the monourea and hemiurea complexes also without any appreciable shifts. In particular, a very strong peak at 1585 cm$^{-1}$ is practically unaltered in its wave number and band shape. Below 400 cm$^{-1}$, no definite correspondence of absorption peaks can be made between these spectra for the same reason as given for copper(II) acetate and its derivatives. By taking into account relative intensities and band shapes, peaks attributable to urea molecules were selected from the spectra of copper(II) caproate monourea and hemiurea in the wave number range 1800—400 cm$^{-1}$.

The absorption spectra of other copper(II) carboxylate hemiureas were recorded and absorptions characteristic of urea molecules were determined.

**Copper(II) Formate Bisurea Dihydrate and Copper(II) Formate Monourea.**—The absorptions of copper(II) formate, copper(II) formate tetrahydrate, copper(II) formate bisurea dihydrate, and copper(II) formate monourea are shown in Table III. In the wave number range 1800—830 cm$^{-1}$, the spectrum of anhydrous copper(II) formate is practically identical with that of the tetrahydrate, although they differ markedly from each other below about 700 cm$^{-1}$. The absorptions of the tetrahydrate appearing in the wave number range 1800—400 cm$^{-1}$ can be found in the

TABLE III. INFRARED ABSORPTIONS (cm$^{-1}$) OF COPPER(II) FORMATE AND ITS DERIVATIVES*

| Copper(II) formate (pale blue modification) | Copper(II) formate tetrahydrate | Copper(II) formate bisurea dihydrate | Copper(II) formate monourea |
|---|---|---|---|
| | | 1675 s | 1668 s |
| | | 1656 s | 1645 s |
| | | 1614 s | 1621 s |
| | | 1592 s | |
| 1562 vs | 1562 vs | 1562 vs | 1581 vs |
| | | | 1513 w |
| | | 1485 m | 1485 m |
| 1384 s | 1384 s | 1379 m | 1389 m |
| | | | 1369 w |
| | | | 1355 m |
| 1366 s | 1366 s | 1361 s | 1343 s |
| | | 1160 w | 1161 w |
| | | 1020 vw | 1048 vw |
| 834 m | 834 m | 834 m | 779 m |
| | | 787 w | 772 m |
| | | 757 w | 738 w |
| | 800—550 br | 591 w | 618 m |
| | | 550 w | |
| | | 512 m | 542 m |
| 423 m | ~390 m | 392 m | ~395 m |
| 343, 330 m | ~308 w | 305 w | |
| ~216 m | ~250 w | ~227 m | ~225 m |

* vw, very weak. br, broad.

TABLE IV. VIBRATIONAL FREQUENCIES OF UREA MOLECULES IN PURE CRYSTALS AND VARIOUS UREA COMPLEXES

| Vibrational mode | Urea (tetragonal) | Urea adducts (hexagonal) | Copper(II) carboxylate monoureas | Copper(II) carboxylate hemiureas | Copper(II) formate bisurea dihydrate |
|---|---|---|---|---|---|
| $NH_2$ stretchings | 3449<br>3436 | 3420<br>3360 | 3420—3500* | ∼3475* | 3440 |
| | 3362<br>3342 | 3240<br>3190 | 3350—3370* | ∼3370 | 3375<br>3240 |
| CO stretching<br>$NH_2$ scissoring | 1681 | 1684<br>1656 | ∼1670 | 1677<br>1661 | 1675<br>1656 |
| | 1629<br>1603 | 1626<br>1597 | ∼1620 | 1626<br>∼1612 | 1614<br>1592 |
| Antisym. CN stretching | 1466 | 1486 | 1468—1485 | ∼1470 | 1485 |
| $NH_2$ rocking | 1156 | 1157 | 1160—1178 | 1170—1175 | 1160 |
| Sym. CN stretching | 1004 | 1015 | ∼1000—1015 | | ∼1020 |
| Out-of-plane skel. deformation | 789 | 794 | ∼780 | ∼775 | 787 |
| $NH_2$ wagging | 715 | 720 | ∼725—738 | | 757 |
| In-plane CO bending | 571 | 608 | 605—618 | 599 | 591 |
| NCN scissoring | 558 | 608 | 535—550 | 534 | 550 |
| $NH_2$ twisting | 530 | 610 | | | 512 |

* Additional weaker bands appearing beyond 3000 cm$^{-1}$ are omitted.

spectrum of copper(II) formate bisurea dihydrate also without any appreciable shift and change in the band contour as shown in Fig. 2.

## Discussion

The absorptions characteristic of carboxylate ions appearing in the wave number range 1800—400 cm$^{-1}$ are almost unaltered by the addition of urea to copper(II) carboxylates except for copper(II) formate and by the substitution of water in copper(II) acetate monohydrate with urea to form copper(II) carboxylate monoureas and hemiureas. In addition, the frequency of absorptions at about 1585 cm$^{-1}$ attributable to the antisymmetric COO stretching vibration is shifted to some extent from the corresponding frequencies observed for sodium, potassium, and silver salts.[4,5] These facts lend additional support to the presumption already suggested by magnetic measurements[1,2] that copper(II) carboxylate monoureas and hemiureas form dimer molecules in crystals.

In the wave number range 1800—400 cm$^{-1}$, the spectrum of copper(II) formate bisurea dihydrate has all absorptions of copper(II) formate tetrahydrate without any appreciable change, in addition to bands attributable to urea molecules. This indicates that the compound forms crystals consisting of two-dimensional network structures as observed by X-ray crystal analysis for the tetrahydrate.[6] On the other hand, copper(II) formate monourea shows a spectral feature quite different from those of copper(II) formate tetrahydrate and bisurea dihydrate. In the first place, the antisymmetric COO stretching frequency at 1581 cm$^{-1}$ is higher than the corresponding frequencies of the tetrahydrate and the bisurea dihydrate by about 20 cm$^{-1}$. Secondly, the COO scissoring vibration appearing at 779 cm$^{-1}$ is lower by about 55 cm$^{-1}$. Lastly, marked splittings of bands are observed in the wave number region of 1389—1343 cm$^{-1}$. These results suggest that the structure of copper(II) formate monourea is basically different from those of copper(II) formate bisurea dihydrate and copper(II) formate tetrahydrate in conformity with a conclusion from magnetic studies[2] that among copper(II) formate and its derivatives, only copper(II) formate monourea forms dimer molecules analogous to those in copper(II) acetate monohydrate in crystals.

The normal vibrations of urea have been calculated and the assignment of observed frequencies has been made by Yamaguchi et al.[7,8] Kutzelnigg et al.[9] have discussed the vibrational spectra of urea molecules in pure crystals and solutions and those constituting the host lattice of urea adducts in relation to intermolecular forces. Based on the results of these investigations, frequencies observed for the urea complexes of copper(II) carboxylates have been assigned to various modes of vibration as shown in Table IV. The frequency observed for copper(II) carboxylate monoureas depends on the kind of carboxylate ions to some extent, whereas that of copper(II) carboxylate hemiureas is almost independent of the chain length of the carboxylate ions.

A urea molecule has an oxygen atom and two nitrogen atoms capable of being coordinated on a

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[5] Y. Kuroda and M. Kubo, *J. Phys. Chem.*, **64**, 759 (1960).

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

[7] A. Yamaguchi, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **78**, 1319, 1467 (1957).

[8] A. Yamaguchi, T. Miyazawa, T. Shimanouchi and S. Mizushima, *Spectrochim. Acta*, **10**, 170 (1957).

[9] W. Kutzelnigg, R. Mecke, B. Schrader, F. Nerdel and G. Kresse, *Z. Electrochem.*, **65**, 109 (1961).

metal atom. It is expected that coordination affects the vibrational frequencies of urea, especially those of $NH_2$ stretching and CO stretching vibrations. In fact, Penland et al.⁽¹⁰⁾ have found that dichloro(bisurea)platinum(II) and dichloro-(bisurea)palladium(II) show a decrease in the frequencies of $NH_2$ stretchings and antisymmetric CN stretching as well as an increase in the frequencies of CO stretching coupled with $NH_2$ scissoring and concluded that nitrogen is involved as donor atoms in coordination. On the other hand, Table IV shows that no marked differences can be found in the $NH_2$ stretchings, the CO stretching mixed with the $NH_2$ scissoring, the antisymmetric CN stretching, etc. between tetragonal or hexagonal urea and the urea complexes of copper(II) carboxylates. Accordingly, it is concluded that urea molecules in these urea complexes are not bonded to copper atoms by coordination bonds having a covalent character but that they are involved in bonding by electrostatic forces or hydrogen bondings as in the tetragonal or hexagonal crystals of urea. Penland et al.⁽¹⁰⁾ have presumed that oxygen-to-metal bonds are formed in the dichloro(bisurea) complexes $M(NH_2CONH_2)_2Cl_2$ of zinc(II) and copper(II) showing no such marked shifts of bands as observed for the platinum(II) and palladium(II) complexes and that two chlorine atoms and two oxygen atoms occupy coordination sites at the corners of a square with a metal atom at its center. However, it is very likely that in dichloro(bisurea)-copper(II), for instance, all the coordination sites of copper are occupied by chlorine, the coordination squares being arranged in a one-dimensional array by sharing their edges as in the crystals of dichloro-(1, 2, 4-triazole)copper(II)⁽¹¹⁾ and that urea molecules are not directly involved in the square coordination of copper.

This paper is dedicated to Professor Masao Kotani of the University of Tokyo in commemoration of his sixtieth birthday.

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

11) J. A. J. Jarvis, *Acta Cryst.*, **15**, 964 (1962).