Crystal Structure of Binuclear Copper(II) Complex with 3-Ethyl-2-pyridone and Magnetism of Its Homologues

Yuzo NISHIDA* and Sigeo KIDA
Department of Chemistry, Faculty of Science, Kyushu University 33, Fukuoka 812
(Received July 14, 1984)

Synopsis. The crystal structure of bis(*N*,*N*-dimethylformamide)tetrakis(3-ethyl-2-pyridonato)dicopper(II) was determined by X-ray diffraction method. Crystal data: Space group $P2_1/n$(monoclinic), a=9.906(1), b=13.494(3), c=14.029(2) Å, β=103.81(1)°. The crystal consists of centrosymmetric binuclear units in which two copper(II) ions are linked by four pyridonate anions similarly to copper(II) acetate monohydrate. The Cu-Cu distance is 2.55 Å. The cryomagnetic data revealed that $-2J$ values are in the range 360—405 cm^{-1} for the series of complexes.

It is well known that copper(II) acetate monohydrate consists of binuclear structure in which two copper(II) ions are bridged by four acetate anions with a short Cu-Cu distance(2.64 Å).[1] Similar structures were also observed for copper(II) complexes with 1,3-diphenyltriazene,[2] 1,7-diazaindene,[3] and adenine.[4] It is also known that 2-pyridone forms binuclear complexed with Ph(II), Mo(II), and Ru(II) ions similar to that of copper(II) acetate monohydrate.[5]

In 1972, Emori *et al.*[6] reported the preparation of Cu(2-pyridonato)$_2$·(2-pyridone), and they assumed that this complex has a structure similar to that of copper(II) acetate monohydrate based on the magnetic property. In this study a series of copper(II) complexes with 2-pyridone and its homologues have been prepared and characterized by the spectral and magnetic measurements. In order to confirm the binuclear structure, the crystal structure of one of them, bis(*N*,*N*-dimethylformamide)tetrakis(3-ethyl-2-pyridonato)dicopper(II) has been determined by X-ray diffraction method.

Experimental

Preparations. 2-Pyridone was obtained commercially. The substituted 2-pyridones were prepared by the published method.[7] The copper(II) complexes were prepared by the following way. A DMF (or DMSO) solution containing substituted 2-pyridone (0.01 mol) and copper(II) hydroxide (0.005 mol) was kept at 50 °C for five hours. From the filtrate, the complex was obtained as dark prisms.[8]

Magnetic Measurements. Magnetic susceptibilities were measured in the temperature range 90—300 K by the published method.[9] Magnetic moments were calculated by the equation, $\mu_{eff}=2.828\sqrt{(\chi-N\alpha)T}$, where χ and $N\alpha$ have usual meanings.[1]

Determination of the Cell Constant and Collection of the Intensity Data. A crystal with the approximate dimension of 0.3×0.2×0.3 mm^3 was used for the determination and the collection of intensity data at 294 K. The cell dimensions and the diffraction intensities were measured on a Rigaku AFC-5 Automatic Diffractometer by using graphite monochromated Mo $K\alpha$ radiation. Crystal data. Cu(3-ethyl-2-pyridonato)$_2$·DMF, FW=380.9, space group $P2_1/n$(monoclinic), a=9.906(1), b=13.494(3), c=14.029(2) Å, β=103.81(1)°, Z=4, D_c=1.39 g cm^{-3}, D_m=1.44 g cm^{-3} (by floatation method). All independent reflections within the range $3°<2\theta<55°$ were collected by the use of $2\theta-\theta$ scan mode with a scanning rate 6°(2θ) min^{-1}. A total 1973 independent reflections with $|F_o|>3\sigma(|F_o|)$ were used for the determination of crystal structure. The data were corrected for the Lorentz and polarization effects.

Structure Determination

The position of the copper atom was obtained from the three dimensional Patterson map. The positions of the other non-hydrogen atoms were located by the Fourier synthesis. There was a disorder in ethylcarbon atom (see Table 1). The structure was refined to R=0.065 for the observed reflections by a block-diagonal least-squares method using anisotropic temperature factors for non-hydrogen atoms. At the final stage of the refinement the difference Fourier map showed only featureless peaks. Anisotropic temperature factors of the non-hydrogen atoms and the complete F_o-F_c data are deposited as Documents No. 8506 at the Office of the Editor of the Bulletin of the Chemical Society of Japan. The final atomic coordinates, and the equivalent isotropic temperature factors are given in Table 1. All the calculations were carried out on a M-200 computer at the Computer Center of Kyushu University using the local version[10] of the UNICS system.[11] The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[12]

Results and Discussion

The perspective drawing of the structure of bis(*N*,*N*-dimethylformamide)tetrakis(3-ethyl-2-pyridonato)dicopper(II) is shown in Fig. 1 with selected bond lengths and bond angles. As has been expected, the crystal consists of centrosymmetric binuclear unit similar to that of copper(II) acetate monohydrate. The Cu-Cu distance is 2.55 Å, which is shorter than that of copper(II) acetate monohydrate (2.64 Å). The DMF molecule coordinates to the copper(II) atom at the apical position, forming a five-coordinated environment around the copper(II) ion.

The magnetic moments are summarized in Table 2. The magnetic moments of the complexes at room temperature are in the range 1.18—1.26 BM, implying that antiferromagnetic interaction is operating between two copper(II) ions. The temperature dependence of magnetic susceptibilities(90—300 K) of these complexes can be interpreted in terms of Bleaney-Bowers equation with the $-2J$, g and $N\alpha$ values listed in the Table 2.

All the electronic spectra of the compounds are similar to each other. In DMF the d-d band and the shoulder were observed at 17.4×10^3 cm^{-1} (log ε=2.41) and

Table 1. Atomic coordinates ($\times 10^4$), their estimated standard deviation (in parentheses) and equivalent isotropic temperature factors

Atom	x	y	z	B_{eq}/Å^2
Cu	96(1)	270(1)	9148(1)	4.3
O1	−652(6)	1522(4)	9496(4)	6.0
O2	−1817(5)	−223(5)	8720(3)	6.4
O3	−21(6)	832(5)	7593(4)	6.5
N1	−799(6)	1093(4)	11038(4)	4.7
N2	−2039(6)	−699(5)	10238(5)	4.8
C1	−978(8)	1763(6)	10287(5)	4.8
C2	−1550(8)	2715(6)	10408(7)	5.6
C3	−1858(9)	2947(7)	11282(7)	6.5
C4	−1661(9)	2240(7)	12051(7)	6.7
C5	−1120(9)	1322(7)	11902(6)	5.8
C6	−1751(10)	3451(6)	9558(7)	6.6
C7	−3119(10)	3243(8)	8808(7)	7.5
C8	−2574(8)	−593(6)	9262(6)	5.0
C9	−3987(9)	−879(8)	8840(7)	7.0
C10	−4771(10)	−1236(8)	9430(8)	7.3
C11	−4219(10)	−1336(7)	10457(7)	6.8
C12	−2862(10)	−1080(6)	10829(7)	5.8
C15	−1166(9)	1217(7)	7246(6)	6.0
N3	−1673(7)	1339(5)	6286(4)	5.6
C16	−882(10)	1011(8)	5577(6)	7.1
C17	−3077(10)	1753(8)	5909(8)	7.5
C13	−4462(17)	−853(17)	7730(11)	12.9
C14A[a]	−4894(25)	−759(15)	7439(16)	7.0
C14B[a]	−5835(20)	−796(20)	7158(15)	8.2

a) 50% probability.

25×10^3 cm^{-1} ($\log\varepsilon\approx2.7$) for bis(*N*,*N*-dimethylformamide)tetrakis(3-ethyl-2-pyridonato)dicopper(II). The shoulder at 25×10^3 cm^{-1} must correspond to 26.6×10^3 cm^{-1} band of copper(II) acetate monohydrate[1] which has been used for diagnosis of the binuclear structure, since the ligand itself has no absorption in this region.

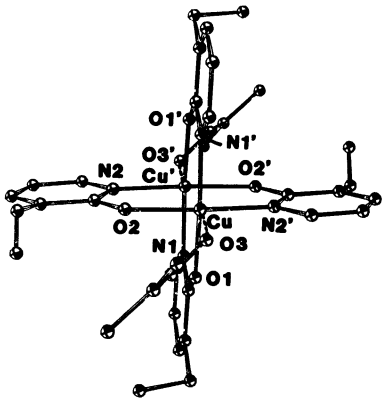

Fig. 1. Perspective drawing of binuclear structure of bis(*N*,*N*-dimethylformamide) tetrakis (3-ethyl-2-pyridonato) dicopper (II). Selected distances (Å): Cu'–Cu=2.550(1); Cu–O1=1.956(6); Cu–O2=1.961(6); Cu'–N1=2.003(6); Cu–N2'=1.997(6); Cu–O3=2.283(6). Selected bond angles (deg): O1–Cu–O2=88.3(3); O1–Cu–N2'=91.5(2); O1–Cu–N1'=171.9(2); O2–Cu–N2'=172.3(2); O2–Cu–O3=89.8(2); O2–Cu–N1'=89.5(2).

Table 2. Magnetic data of complexes

Complex	μ_{eff}/BM[a]	$-2J$/cm^{-1}[b]
$[Cu_2(pyr)_4(dmf)_2]$[c]	1.24	365
$[Cu_2(pyr)_4(dmso)_2]$	1.26	360
$[Cu_2(3\text{-methyl-pyr})_4(dmf)_2]$	1.18	405
$[Cu_2(4\text{-methyl-pyr})_4(dmf)_2]$	1.20	400
$[Cu_2(3\text{-ethyl-pyr})_4(dmf)_2]$	1.22	395

a) 295 K. b) $-2J$ values were determined so that the experimental $\chi-T$ curves are simulated by Bleaney-Bowers equation ($g=2.15$, $N\alpha/10^{-6}$ cgs mol$^{-1}=60$, cgs mol$^{-1}\times4\pi\times10^{-6}\rightarrow$m^3 mol^{-1}). c) (pyr) represents 2-pyridonate anion.

References

1) M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).
2) R. L. Martin and H. Waterman, *J. Chem. Soc.*, **1959**, 1359.
3) R. W. Brooks and R. L. Martin, *Inorg. Chem.*, **14**, 528 (1975).
4) A. Terziz, A. N. Beauchamp, and R. Rivest, *Inorg. Chem.*, **12**, 1166 (1973).
5) F. A. Cotton and R. A. Walton, "Multiple Bonds between Metal Atom," John Wiley & Sons, New York (1982).
6) S. Emori, I. Okano, and Y. Muto, *Bull. Chem. Soc. Jpn.*, **45**, 3717 (1972).
7) O. Seide, *Ber.*, **57**, 793, 1805 (1924).
8) The analytical data of the new compounds were deposited to the Editor of the Bulletin of the Chemical Society of Japan.
9) W. Kanda, H. Okawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **57**, 1159 (1984).
10) S. Kawano, *Rep. Comp. Cent. Kyushu Univ.*, **13**, 39 (1980).
11) "Universal Crystallographic Computer Program System(UNICS)," ed by T. Sakurai, The Crystallographic Society of Japan, Tokyo (1964).
12) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham (1962).