Inorganica Chimica Acta, *158* (1989) 217–220

Structure of Bis(2,6-dimethylpyridine)copper(I) Perchlorate. The Relationship Between the Cu–N(pyridine) Distance and Cu···CH_3(methyl group) Contacts

MEGUMU MUNAKATA*, SUSUMU KITAGAWA, HISAO SHIMONO

Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka 577, Japan

and HIDEKI MASUDA

Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

(Received August 17, 1988)

Abstract

One of the conformational polymorphs of bis(2,6-dimethylpyridine)copper(I) perchlorate has been synthesized and its structure determined by single-crystal X-ray diffraction techniques. The crystals are monoclinic, space group I_a, with $a = 14.858(3)$, $b = 8.236(1)$, $c = 16.308(2)$ Å, $\beta = 124.78(1)^\circ$, $Z = 4$; R was 0.070 for $N_o = 1160$ independent observed reflections. The coordination geometry around the Cu(I) atom is nearly linear with different Cu–N distances, Cu–N(1) = 1.899(16) and Cu–N(2) = 1.953(22) Å. The dihedral angle between the pyridine planes is 56.2. The relationship between the Cu–N-(pyridine) distance and Cu···CH_3(methyl group) contacts has been discussed.

Introduction

Few complexes of d^{10} metal ions are known with a coordination number of 2. They are generally limited to the +1 ions of the Group IB metals and the closely related Hg(II) species [1]. Examples [1–3] are $[Ag(NH_3)_2]^+$, $[CuCl_2]^-$, $[AgCl_2]^-$, $[Ag(CN)_2]^-$, $[Au(CN)_2]^-$ and $[Hg(CN)_2]^-$. The geometry of coordination number 2 would be expected to be linear, either from the point of view of simple electrostatics or from the use of sp hybrids by the metal. Orgel [4] has suggested that since the $(n-1)$d orbitals in these metals have nearly the same energy as the ns and np orbitals, the d_{z^2} orbitals can enter into this hybridization to remove electron density from the region of the ligands. Recently, complexes of two-coordinate copper(I) ion with ligands except for ammine, cyanide and halide ions were synthesized. The copper atoms of a dinuclear copper(I) complex with *N,N,N′,N′*-tetrakis(2-benzimidazolylmethyl)-1,2-ethanediamine [5] and mononuclear copper(I) complex with 1,7-bis(2-benzimidazolyl)-2,6-dithiaheptane [6] are linearly coordinated by two benzimidazole nitrogen atoms. Two-coordinate copper complexes with 1-methylpyrazole and 1,3,5-trimethylpyrazole [7] show an approximately linear N–Cu–N geometry with short Cu–N bond lengths. A number of bis(pyridine derivatives)copper(I) perchlorate and nitrate derivatives have been prepared by the reduction of the copper(I) salt by electrolytic copper in acetonitrile and their structures have been established by X-ray crystallography [8]. Crystals of bis(2,6-dimethylpyridine)copper(I) perchlorate (polymorph 1) are monoclinic, space group $C2/c$ [8]. The cation lies with the copper atom on a crystallographic inversion center; Cu–N = 1.936(5) Å and N–Cu–N = 180°. In methanol, we have prepared a conformational polymorph (polymorph 2) of the bis(2,6-dimethylpyridine)copper(I) perchlorate of which crystals are monoclinic space group I_a. The crystal structure in this paper was determined by a single crystal structrue analysis and the relationship between the Cu–N-(pyridine) distance and Cu···CH_3(methyl group) contacts is discussed.

Experimental

Preparation

Copper(II) diperchlorate hexahydrate (46.3 mg, 0.125 mmol) in methanol (2.5 cm^3) was reduced with copper wire to copper(I) under ethylene ($Cu^{2+} + Cu \rightleftharpoons 2Cu^+$). To the reaction solution, a methanol solution (2 cm^3) of 2,6-dimethylpyridine (0.5 mmol, 0.058 cm^3) was added to form the complex $[Cu(2,6\text{-}Me_2py)_2]ClO_4$ (2,6-Me_2py = 2,6-dimethylpyridine). The solution containing the precipitates of the complex was sealed in a glass tube under ethylene and the precipitates were dissolved completely at 30 °C. After two days, pale yellow crystals were obtained from this solution at −10 °C.

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[*] Author to whom correspondence should be addressed.

0020-1693/89/$3.50

^1H NMR Spectroscopy

Proton NMR spectra were obtained in $(CD_3)_2CO$ at 200 MHz with a Jeol FX-200 NMR spectrometer and chemical shifts are given in ppm relative to tetramethylsilane as internal reference.

Crystallography

A pale yellow needle crystal with the approximate dimensions of *ca.* 0.3 X 0.3 X 0.2 mm was used for the determination and the collection of intensity data at 296 K. The cell dimensions and the diffraction intensities were measured on a Rigaku AFC-6B diffractometer by using graphite monochromated Cu Kα radiation (λ = 1.54178 Å), μ = 35.51 cm^{-1}.

Crystal Data

$C_{14}H_{18}ClCuN_2O_4$, formula weight = 377.29, space group I_a (monoclinic), a = 14.858(3), b = 8.236(1), c = 16.308(2) Å, β = 124.78(1)°, Z = 4, D_c = 1.529 g cm^{-3}. All independent reflections within the range of $2\theta < 120°$ were collected by the use of ω–2θ scan mode and a scanning rate of 8° min^{-1}. Three reflections were monitored every 60 reflections. There was no significant variation of the intensties during data collection. The intensity data were converted to F_o data in the usual manner. No absorption correction was applied. The standard deviations, $\sigma(F_o)$, were estimated by counting statistics. A total of 1160 independent reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the determination of the crystal structure.

Structure Determination

The structure was solved by the heavy-atom method and refined by block-diagonal least-squares refinement. Several cycles of the refinement including anisotropic thermal parameters were carried out with the weighting scheme, $w = 1/\sigma^2(F_o)$. Atomic scattering factors and anomalous dispersion terms were taken from ref. 9. The hydrogen atoms were included and refined as being isotropic in the last cycle; their positions were obtained from the Fourier difference synthesis. The final R and R' values were 0.070 and 0.069, respectively. The final Fourier difference map showed no significant features. All calculations were performed on a FACOM M-382 computer at the Data Processing Center of Kyoto University using the program system KPPXRAY [10]. Crystal data of polymorphs 1 and 2 are given in Table 1. The atomic parameters are given in Table 2. Bond distances and interbond angles are listed in Table 3.

TABLE 1. Crystal Data

	Polymorph 1	Polymorph 2
Formula	$C_{14}H_{18}ClCuN_2O_4$	$C_{14}H_{18}ClCuN_2O_4$
M	377.3	377.3
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	I_a
a (Å)	15.175(6)	14.858(8)
b (Å)	8.151(3)	8.236(1)
c (Å)	13.227(10)	16.308(2)
β (°)	99.26(4)	124.78(1)
U (Å^3)	1615(1)	1639.1
D_c (g cm^{-1})	1.56	1.53
Z	4	4
2θ max (°)	50	120
N_o	724	1160
R	0.045	0.070
R'	0.047	0.069
μMo (cm^{-1})	14.6	
μCu (cm^{-1})		35.5

TABLE 2. Final Atomic Coordinates for $[Cu(2,6\text{-}Me_2py)_2]ClO_4$ (polymorph 2)[a]

Atom	x	y	z
Cu	0.7502(5)	0.1295(3)	0.9996(4)
Cl	0.7520(10)	0.6148(4)	1.0027(8)
C(1)	0.8931(9)	0.1670(15)	0.9349(7)
C(2)	0.9251(10)	0.1538(21)	0.8701(11)
C(3)	0.8634(14)	0.0630(25)	0.7907(12)
C(4)	0.7649(15)	0.0215(24)	0.7610(12)
C(5)	0.7304(10)	0.0441(20)	0.8230(9)
C(6)	0.9626(14)	0.2662(22)	1.0323(12)
C(7)	0.6166(14)	−0.0195(27)	0.7882(12)
C(8)	0.5981(14)	0.1918(24)	1.0480(13)
C(9)	0.5663(14)	0.1615(30)	1.1147(12)
C(10)	0.6372(13)	0.0949(24)	1.2148(12)
C(11)	0.7357(14)	0.0209(26)	1.2389(11)
C(12)	0.7786(17)	0.0349(25)	1.1809(12)
C(13)	0.5383(12)	0.2510(25)	0.9591(11)
C(14)	0.8801(14)	−0.0149(30)	1.2004(12)
N(1)	0.7918(8)	0.1193(14)	0.9124(7)
N(2)	0.7049(11)	0.1022(21)	1.0935(10)
O(1)	0.8198(16)	0.6934(34)	0.9890(21)
O(2)	0.7089(15)	0.7228(23)	1.0297(12)
O(3)	0.7805(20)	0.4712(23)	1.0482(15)
O(4)	0.6513(15)	0.5762(28)	0.9033(11)

[a] e.s.d.s given in parentheses.

Results and Discussion

The atomic labelling scheme for polymorph 2 of $[Cu(2,6\text{-}Me_2py)_2]ClO_4$ is shown in Fig. 1. The distance between neighboring pyridine rings is 3.49 Å, as shown in Fig. 2. The coordination geometry around the Cu(I) atom is nearly linear with different Cu–N distances, Cu–N(1) = 1.899(16) and Cu–N(2) = 1.953(22) Å. The average Cu–N distance of 1.926(22) Å is substantially equal to that of 1.936(5) Å in polymorph 1 and is at the longer end of the range (1.86(1)–1.936(5) Å) reported for two-coordinate copper(I) complexes with nitrogen donor atoms (Table 4). The Cu–N bond distance increases

TABLE 3. Selected Bond Distances (Å) and Angles (°) for $[Cu(2,6\text{-}Me_2py)_2]ClO_4$ (polymorph 2)

Cu–N(1)	1.899(16)
Cu–N(2)	1.953(22)
C(1)–N(1)	1.359(16)
C(5)–N(1)	1.365(19)
C(8)–N(2)	1.390(28)
C(12)–N(2)	1.315(21)
Cu–O(3)	2.911(20)
N(1)–Cu–N(2)	171.0(7)
Cu–N(1)–C(1)	123.5(9)
Cu–N(1)–C(5)	122.2(12)
Cu–N(2)–C(8)	115.2(14)
Cu–N(2)–C(12)	120.9(16)
C(1)–N(1)–C(5)	123.5(9)
C(8)–N(2)–C(12)	115.2(14)

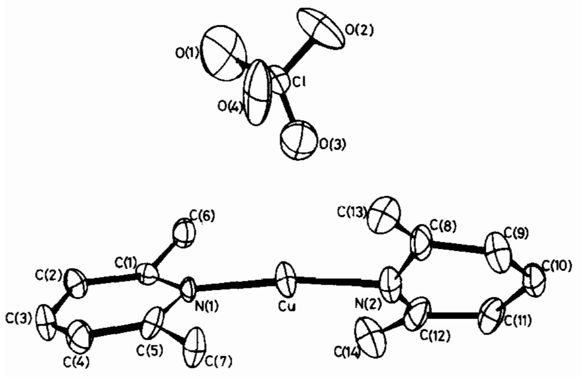

Fig. 1. Molecular structure of $[Cu(2,6\text{-}Me_2py)_2]ClO_4$ (polymorph 2). Atoms are represented by thermal ellipsoid at the 20% probability level.

in the order $[Cu(2,6\text{-}Me_2py)_2]ClO_4 < [Cu(2\text{-}Mepy)_3]ClO_4$ (1.99 Å) [14] $< [Cu(py)_4]ClO_4$ (2.046(4) Å) [13]. The N(1)–Cu–N(2) angle is 171.0(7)° which is slightly longer than 180° of polymorph 1 of $[Cu(2,6\text{-}Me_2py)_2]ClO_4$.

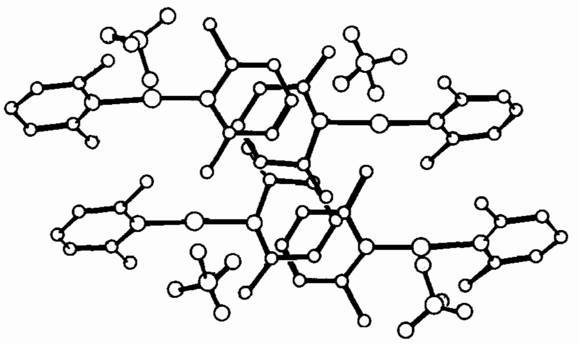

Fig. 2. View showing the stacking interaction between $2,6\text{-}Me_2py$ ligands.

The most striking feature of polymorph 2 is that the dihedral angle between the pyridine planes is 56.2°, whereas the dihedral angle for polymorph 1 is 0. Intramolecular contacts between methyl groups are apparently negligible, being C(7)–C(14) = 4.35(4) and C(6)–C(13) = 4.18(4) Å. As previously described, two-coordinate copper(I) complexes with 1-methylpyrazole (1-Mepz) and 1,3,5-trimethylpyrazole ($1,3,5\text{-}Me_3pz$) show an approximately linear N–Cu–N geometry with a short Cu–N(pyrazole) bond length of 1.87 Å. The dihedral angle between the pyrazole planes for $[Cu(1\text{-}Mepz)_2]BF_4$ and $[Cu(1,3,5\text{-}Me_3pz)_2]BF_4$ are 4.7° and 8.7°, respectively. It has been considered that this short Cu–N bond distance does not result from back-bonding from Cu(I) to pyrazole-π^*, but rather from strong σ-overlap between the copper and the ligand because a significant back-bonding interaction would dictate that the pyrazole ring be mutually perpendicular in order to maximize delocalization of the d electrons on copper. This is supported by the fact that the average Cu–N(pyridine) distance of polymorph 2 is substantially equal to that of polymorph 1 in spite of the large difference in the dihedral angle between the pyridine ring. At least this is not an important factor by which the Cu–N bond distance is significantly affected.

TABLE 4. Geometrical Parameters of Two-coordinate Copper(I) Complexes with Nitrogen Donor Atoms

	Cu–N (Å)	N–Cu–N (°)	θ (°)	Cu···CH_3 (Å)	Reference
$[Cu_4(NMe\text{–}N{=}NMe)_4]$	1.87(3) (mean)	172.5(mean)			11
$[Cu_2(NPh\text{–}N{=}NPh)_2]$	1.898(18)–1.939(18)	172			12
$[Cu_2(EDTB)](ClO_4)_2$	1.869(4)–1.876(4)	170.9			5
$[Cu(2,6\text{-}Me_2py)_2]ClO_4$	1.936(5)	180.0	0	3.042(mean)	8
$[Cu(2,6\text{-}Me_2py)_2]ClO_4$	1.879(16), 1.953(22)	171.0	56.2	2.996(mean) 3.060(mean)	this work
$[Cu(2,4\text{-}Me_2py)_2]ClO_4$	1.86(1)	170	58	3.099(mean)	8
$[Cu(BBDHp)](PF_6)_{0.66}(BF)_{0.34}$	1.918(4)	168.5	80.5		6
$[Cu(1\text{-}Mepz)_2]BF_4$	1.873(3), 1.879(3)	178.2	4.7	3.200(mean)	7
$[Cu(1,3,5\text{-}Me_3pz)_2]BF_4$	1.863(4), 1.878(3)	173.8	8.7	3.224(mean)	7

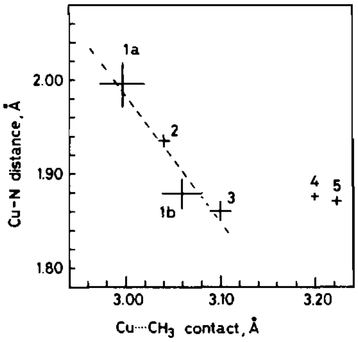

Fig. 3. Correlation between Cu–N distances (Å) and Cu··· CH_3(methyl) contact (Å) in the two-coordinate copper(I) complexes. 1a and 1b, $[Cu(2,6\text{-}Me_2py)_2]ClO_4$ (polymorph 2); 2, $[Cu(2,6\text{-}Me_2py)_2]ClO_4$ (polymorph 1) [8]; 3, $[Cu(2,4\text{-}Me_2py)_2]ClO_4$ [8]; 4, $[Cu(1\text{-}Mcpz)_2]BF_4$ [7]; 5, $[Cu(1,3,5\text{-}Me_3pz)_2]BF_4$ [7].

On the other hand, the contact between the methyl groups and copper atom affects the Cu–N bond distances in polymorph 2. The contacts of Cu···C(13) (3.038(23) Å) and Cu···C(14) (2.953(20) Å) in the 2,6-Me_2py having the long Cu–N(2) bond distance are shorter than those of Cu···C(6) (3.044(22) Å) and Cu···C(7) (3.075(18) Å) in the other 2,6-Me_2py having the short Cu–N(1) bond distance. Figure 3 shows the correlation between Cu–N distances and Cu···CH_3(methyl group) contacts for two-coordinate copper(I) complexes with 2,4-, and 2,6-dimethylpyridine and illustrates that the Cu–N distance lengthens as the Cu···CH_3 contacts shorten. It is noted that the Cu···CH_3 contacts (2.953–3.075 Å) are nearly equal to 3.03 Å of the sum of the C–H bond distance of 1.1 Å, the van der Waals radius of the H atom (1.2 Å) and the ionic radius of the Cu(I) atom (0.73 Å) [15]. The copper(I) complexes with 1-methylpyrazole and 1,3,5-trimethylpyrazole deviate from the correlation because of the difference in the basicity and structure between the pyridine ring and the pyrazole ring. In conclusion, the Cu–N(2) bond distance of two-coordinate copper(I) complexes having pyridines substituted at the 2- and/or 6-positions by methyl groups is governed by the steric repulsion between the methyl groups and the copper atom.

2,6-Dimethylpyridine in acetone-d_6 solution at −90 °C exhibits ^{1}H NMR signals at 2.42(s), 7.08(d) and 7.59(t) ppm which are assigned to methyl-protons, 3-H and 4-H, respectively. The ^{1}H NMR signals corresponding to singles species of 2,6-Me_2py in $[Cu(2,6\text{-}Me_2py)_2]ClO_4$ were observed at 3.00(s), 7.64(d) and 8.13(t) ppm indicating either two equivalent 2,6-Me_2py or a rapid exchange between two non-equivalent 2,6-Me_2py in solution.

Supplementary Material

For $[Cu(2,6\text{-}Me_2py)_2]ClO_4$: tables of atomic parameters for non-hydrogen atoms, fractional coordinates, isotropic thermal parameters for hydrogen atoms, anisotropic thermal parameter for non-distances torsion angles, bond angles, bond distances torsion angles and observed and calculated structure factors are available from the author on request.

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