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Short Communication

Synthesis, Structure and Characterization of the Binuclear Copper(II) Complex $[Cu(C_6H_5COO)_2(C_5H_6N_2)]_2 \cdot (C_4H_8O)_2$

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Binuclear copper complexes are very important in coordination chemistry and catalytic reactions. Certain copper complexes have been shown to have unusual chemical properties of importance in such diverse areas as oxygen transfer, oxidative addition and homogenous hydrogenation.[1] To obtain insight into the correlation between the structure and nature of copper proteins, low-molecular-weight coordination compounds may be used to model these copper proteins.[2] The electronic structure and bonding at copper proteins can be profitably pursued by studying model complexes. These considerations prompted efforts to develop easy methods for the synthesis of binuclear copper complexes which would possess novel coordination chemistry.

This report concerns an oxidative preparation method for a dinuclear copper(II) complex and the X-ray structure analysis of the title complex. It also describes a detailed study of the spectroscopic properties of the title compound.

Experimental

Materials. Reactions were carried out under nitrogen using standard Schlenk line techniques. Solvents were purified by usual methods. The ligand 2-aminopyridine was purchased from Aldrich. The copper powder and other reagents were of high purity and were used as obtained.

Preparation. 2-Aminopyridine (1 mmol, 94 mg) was added to a mixture of dibenzoyl peroxide (1 mmol, 242 mg) and copper powder (1 mmol, 63.5 mg) in a mixed solvent of acetone (20 ml) and tetrahydrofuran (20 ml). The solution was stirred for 48 h at room temperature. The resulting green solution was filtered and left to yield green crystals. They were washed and dried *in vacuo*. Yield: 70%. Found: C, 58.31; H, 5.01; N, 5.79; Cu, 13.12. Anal. Calc: C, 58.54; H, 5.09; N, 5.94; Cu, 13.47%.

Physical measurements. Elemental analyses (C, H and N) were carried out using a REBA-1106 instrument. IR spectra were recorded on a Nicolet 170SX IR spectrophotometer. Copper was determined on a JA96-970 spectrometer. TG-DTA spectra were recorded on a PE-TGS-2 instrument. The room-temperature magnetic susceptibility was measured by using a FH-2 Gouy magnetic susceptibility balance. The molecular weight was measured on a Corona-117 analyser.

Unit-cell dimensions and intensity data were measured at room temperature on an automatic Enraf-N CAD-4 diffractometer using a graphite monochromator and Mo K_α radiator ($\lambda = 0.710173$ Å). The intensities were corrected for Lorentz, polarization and absorption effects, and the structure was solved by direct methods and Fourier syntheses. Positional and thermal parameters were refined by block-diagonal and full-matrix least-squares methods. Hydrogen atoms were included using the weighting function $w = 1/[\sigma^2(F_o) + gF_o^2]$. Computations were performed using the SPD program on an P2P11/44 computer. Figure 1 shows a perspective drawing of the title complex. Details of the crystal data and intensity collection are summarized in Table 1. Atomic parameters and equivalent isotropic thermal parameters of non-H atoms for the complex are given in Table 2. Tables 3 and 4 give selected bond distances and angles, respectively.

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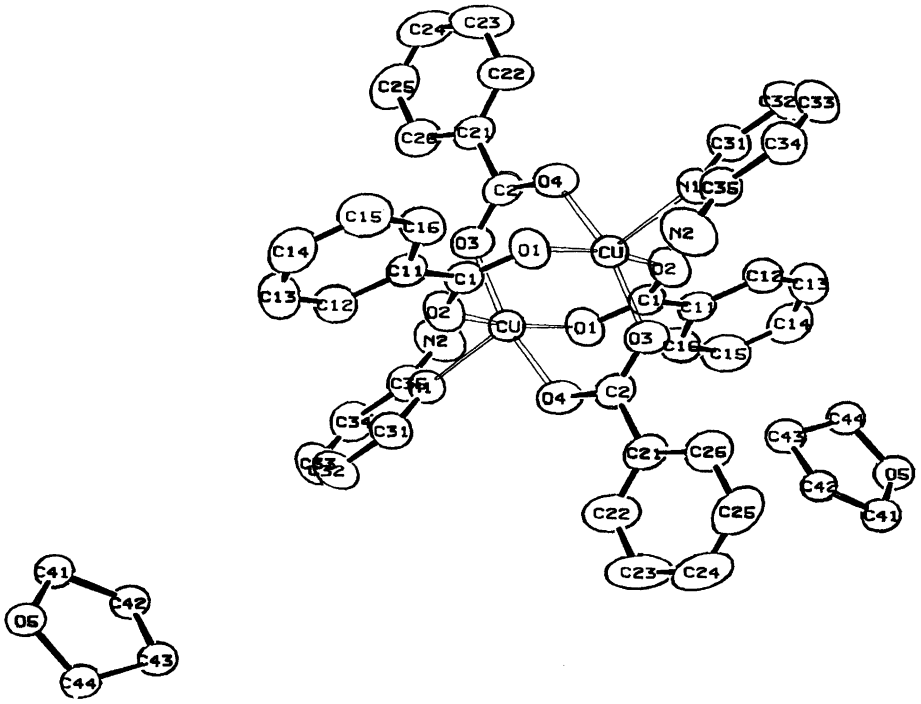

Fig. 1. An ORTEP drawing of the title compex.

Table 1. Crystal and experimental data.

Compound	$C_{46}H_{48}N_4O_{10}Cu_2$
Colour; habit	Green; cuboid
Space group	P_1; triclinic
Unit-cell dimensions	a=10.806(1) Å, α=71.99(2)°
	b=11.169(3) Å, β=89.38(1)°
	c=11.729(2) Å, γ=81.37(1)°
Volume	V=1330.1 Å^3
Z	1
Formula weight	943.93
Density (calcd.)	1.172 g cm^{-3}
Absorption coefficient	8.5 cm^{-1}
F(000)	490
2θ Range	2–50°
Scan type	θ/2θ
Scan speed	4° min^{-1}, in ω
Scan range (ψ)	1.0° plus $K\alpha$-separation
Background measurement	Stationary crystal and stationary counter at beginning and end of scan
Standard reflections	3 measured every 50 reflections
Reflections collected	4921
Independent reflections	3671 [$I > 3.0\sigma(I)$]
Final R-indices (obs. data)	R=0.043, Rw=0.049
Weighting function	$W = 1/[\sigma^2(F_o) + gF_o^2]$

Table 2. Positional parameters and standard deviations

Atom	x	y	z	B/Å^2
Cu	−0.3955(5)	−1.0331(5)	0.98599(5)	3.14(1)
O1	−0.1966(3)	−0.0359(3)	1.0479(3)	4.23(7)
O2	−0.1313(3)	0.13461(3)	1.0699(3)	4.41(8)
O3	−0.244(3)	0.1843(3)	0.8463(3)	4.38(8)
O4	−0.0892(4)	0.0128(3)	0.8235(3)	4.72(8)
O5	0.4214(4)	0.4572(4)	0.7663(3)	5.9(1)
N1	−0.0999(4)	−0.2678(3)	0.9538(3)	3.53(8)
N2	−0.2003(5)	−0.3297(4)	1.1318(4)	5.9(1)
C1	−0.2123(4)	0.0654(4)	1.0767(4)	3.3(1)
C2	−0.0705(4)	0.1264(4)	0.7850(4)	3.6(1)
C11	−0.3376(4)	0.1046(4)	1.1193(4)	3.4(1)
C12	−0.3594(5)	0.2104(4)	1.1590(4)	4.3(1)
C13	−0.4763(6)	0.2479(5)	1.1960(5)	5.4(1)
C14	−0.5731(5)	0.1835(6)	1.1901(5)	5.6(1)
C15	−0.3155(5)	0.0785(5)	1.1514(5)	5.5(1)
C16	−0.4350(5)	0.0386(5)	1.1170(4)	4.4(1)
C21	−0.1053(5)	0.1974(4)	0.6568(4)	3.9(1)
C22	−0.1528(7)	0.1387(5)	0.5840(5)	6.7(2)
C23	−0.1829(8)	0.2030(6)	0.4645(5)	8.1(2)
C24	−0.1684(7)	0.3270(6)	0.4173(5)	6.6(2)
C25	−0.1218(6)	0.3867(5)	0.4876(5)	6.2(2)
C26	−0.0896(5)	0.3224(5)	0.6080(5)	4.9(1)
C31	−0.0615(5)	−0.2901(4)	0.8510(5)	4.4(1)
C32	−0.0852(6)	−0.3943(5)	0.8209(5)	5.7(1)
C33	−0.1488(6)	−0.4801(5)	0.8991(5)	6.1(1)
C34	−0.1903(5)	−0.4590(4)	1.0009(5)	5.2(1)
C35	−0.1649(5)	−0.3499(4)	1.0281(5)	4.1(1)
C41	0.4691(7)	0.4701(7)	0.6618(5)	6.7(2)
C42	0.5947(8)	0.395(1)	0.6809(7)	12.6(3)
C43	0.6070(8)	0.3147(7)	0.8034(6)	8.8(2)
C44	0.5162(7)	0.3817(7)	0.8643(6)	7.6(2)

Results and discussion

The direct use of metallic copper powder and dibenzoyl peroxide is characteristic of the present synthetic method, which is significantly different from previous preparations of the binuclear copper(II) compex. The compex is stable in air at room temperature, and it begins to decompose when heated to 23 °C. It is easily soluble in acetone, ethanol and methanol, and sparingly soluble in benzene. Its molar conductivity (5.3 S cm^2 mol^{-1}) in acetone shows

Table 3. Selected bond lengths (in Å)

Cu–O1	1.977(3)	Cu–O4	1.972(3)	Cu–N1	2.178(4)
O1–C1	1.265(6)	O2–C1	1.250(6)	O3–C2	1.255(7)
O4–C2	1.255(5)	O5–C41	1.407(7)	O5–C44	1.407(7)
N1–C31	1.353(7)	N1–C35	1.334(6)	N2–C35	1.346(7)
N2–H1	0.941(5)	N2–H2	0.850(4)	C1–C11	1.489(6)
C2–C21	1.490(6)	C11–C12	1.386(7)	C11–C16	1.387(8)
C12–C13	1.379(8)	C13–C14	1.369(9)	C14–C15	1.370(9)

Table 4. Selected bond angles (in °)

O1–Cu–O4	90.1(1)	O1–Cu–N1	98.7(1)	O4–Cu–N1	94.6(1)
Cu–O1–C1	124.1(3)	Cu–O4–N2	124.5(3)	C41–O5–C44	108.3(5)
Cu–N1–C31	115.6(3)	Cu–N1–C35	126.0(4)	C31–N1–C35	118.3(4)
C35–N2–H1	117.9(4)	C35–N2–H2	121.0(5)	O1–C1–O2	124.9(4)
O1–C1–C11	117.4(4)	O2–C1–C11	117.7(4)	O3–C2–O4	125.0(4)
O3–C2–C21	117.6(4)	O4–C2–C21	117.3(5)	C1–C11–C12	120.6(5)
C1–C11–C16	120.7(5)	C12–C11–C16	118.7(5)	C11–C12–C13	120.4(5)
C12–C13–C14	120.2(6)	C13–C14–C15	120.1(5)	C14–C15–C16	119.8(6)

that it is a nonelectrolyte there and exists as a molecule.[3] The title complex is paramagnetic at room temperature ($\mu_{eff} = 1.45$ for single copper) showing an antiferromagnetic interaction, which is usually found for this type of binuclear copper(II) compound.[4] The thermogravimetric curve title compex shows, in the 154–583 °C temperature range, a pronounced weight loss due to the total combustion to the organic matter, giving CuO as final residue. The measured molecular weight is 945 (calc. 943).

The IR data of the title compound shows the existence of the bridging benzoato through the observation of characteristic absorption bands (1600–1400, 950–700, 500–600 cm^{-1}). The $\nu_{a(COO)}$ and $\nu_{s(COO)}$ of the title complex are 1570 and 1402 cm^{-1}, respectively. In the range 950–700 and 500–600 cm^{-1}, the characteristic absorption bands of $\delta_{(COO)}$ and $\pi_{(COO)}$, respectively, disappear. These are the characteristics of a typical bridging coordination benzoate.[5] In the complex, the bands due to ν_{NH} stretching and δ_{NH} bending of 2-aminopyridine are almost the same as those of the free ligand. According to this fact, we suggest that the nitrogen atom of NH_2 does not coordinate to the central ion. This is consistent with the result of the crystal structure.

The complex has the expected dimeric form with two copper(II) atoms surrounded by four benzoate groups and two 2-aminopyridine ligands. This binuclear copper(II) molecule possesses a centre of symmetry (except tetrahydrofuran). The Cu and the carboxyl O's, are in the range 1.972(3)–1.977(3) Å [av. 1.974(3)]. The N1 atom in 2-aminopyridine group gives a significantly longer distance from Cu, av. 2.178(4) Å, than the coordinated O's. The four O atoms and N1 atom form a distorted square pyramid with the N1 atom to 2-aminopyridine at the apical position. The basal plane (the four oxygens of the bridging benzoate ligands) forms an almost perfect square. The octahedral environment about the copper is completed by the other copper atom of the dimer. The four C–O distances in the two carboxyl bridges are not significantly different [av. 1.255(6) Å].

There have been many structural reports concerning bridged binuclear copper(II) compounds [6,7] similar to the present complex. The Cu–Cu distance of the present compound is 2.641 Å, which is comparable to that in tetrakis(μ-formato-*O,O'*)-bis(γ-picoline)dicopper(II), 2.665(1) Å.[7]

The Cu atom is coordinated by five atoms: four of them belong to bridging carboxyl groups and one N1 atom to 2-aminopyridine. Tetrahydrofuran exists in the crystal grating as molecular solvent. Two benzoate groups and two 2-aminopyridine ligands are respectively located on the opposite sides to minimise repulsion between the ligands.

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