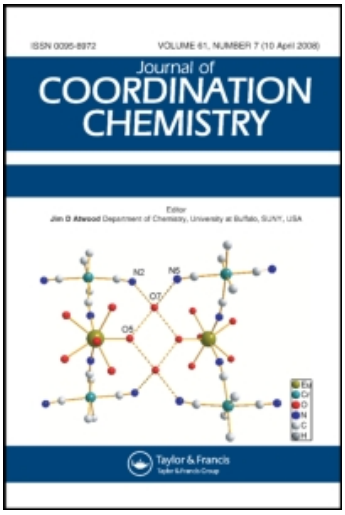

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Synthesis, Crystal Structure and Magnetic Property of Copper(II) Complex with 4'-Cyanobenzyl-1-imidazol

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SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTY OF COPPER(II) COMPLEX WITH 4′-CYANOBENZYL-1-IMIDAZOL

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A neutral mononuclear complex $[Cu(cbIm)_4(NO_3)_2]$ (cbIm = 4′-cyanobenzyl-1-imidazol) was synthesized and characterized by x-ray crystallography. It crystallizes in the triclinic space group P-1 with $a = 8.249(2)$, $b = 8.735(2)$, $c = 16.597(2)$ Å, $\alpha = 81.980(10)$, $\beta = 88.540(10)$, $\gamma = 63.570(10)^\circ$ and $Z = 2$. The final refinement of the structure leads to R and Rw of 0.0394 and 0.0991, respectively. The crystal structure of the complex indicates a distorted octahedral environment around the Cu(II) atom, coordinated by four imidazole N atoms of four cbIm and two O atoms of two nitrates. Magnetic measurements show that the complex exhibits Curie behavior.

Keywords: Copper(II) complex; 4′-Cyanobenzyl-1-imidazol; Crystal structure; Magnetic property

INTRODUCTION

Supramolecular complexes with specific topology and interesting properties can be obtained by assembly of transition metal ions with designed organic ligands [1–3]. Both imidazole and cyano groups are useful functional groups for coordination to metal ions [4–10]. Polyrotaxane, cage-like complexes have been obtained by reaction of imidazole-containing ligands with metal ions [4–6]. On the other hand, honeycomb and hinge-like coordination networks have been reported through coordination of cyano group to metal ions [7–10]. However, no transition metal complexes with ligands having both imidazole and cyano groups have been reported. Investigating reactions of ligands containing imidazole and cyano groups with transition metal ions would be interesting. Recently we prepared 4′-cyanobenzyl-1-imidazol (cbIm) as an organic ligand, and the compound $[Cu(cbIm)_4(NO_3)_2]$ was synthesized by reaction of cbIm with copper(II) nitrate.

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EXPERIMENTAL

Materials and Physical Measurements

The ligand cbIm was prepared according to procedures reported previously [11]. Other reagents were commercially available and used as received without purification. Magnetic susceptibility was measured on a CHAN-2000 Faraday magnetometer in the $75 \sim 300$ K temperature range. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms, and the magnetic moments were calculated using the equation $\mu = 2.828(\chi_M \cdot T)^{1/2}$.

Preparation of $[Cu(cbIm)_4(NO_3)_2]$

12.1 mg (0.05 mmol) $Cu(NO_3)_2 \cdot 3H_2O$ in 5 mL water was added to a 10 mL acetonitrile solution of cbIm (18.3 mg, 0.1 mmol) with stirring at 50°C, and then methanol was added to give clear solution. Single crystals suitable for x-ray diffraction were obtained by slow diffusion of diethyl ether into the clear solution for several days.

Crystal Structure Determination

X-ray diffraction measurements for the title complex were performed on a Siemens P4 automatic four-circle diffractometer using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). Intensity data were collected in the variable ω-scan mode. The structure was solved by a direct method using SHELXS-97 [12] and refined by a full-matrix least-squares calculation on F^2 with SHELXL-97 [13]. All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were generated geometrically. Calculations were performed on a PC-586 computer using the Siemens SHELXTL program package [14,15].

The significant crystal data, details of data collection, and structure refinement are summarized in Table I. Final positional and thermal parameters are listed in Table II, and selected bond distances and angles are given in Table III.

RESULTS AND DISCUSSION

Description of Crystal Structure

The x-ray crystal structure of the title complex indicates that only the imidazole group coordinates with the copper(II) atom and the cyano group of the ligand stays free of coordination. Hence, a mononuclear copper(II) complex was obtained. An ORTEP plot [16] of the complex is shown in Fig. 1. The Cu(II) atom is coordinated by four N atoms of imidazole of four different cbIm ligands. The four N atoms of N1, $N1^{\#4}$, N4, $N4^{\#4}$ (symmetry code: $2-x, -y, -z$) and the Cu atom are strictly coplanar since the mean plane deviation is 0 Å. The distance of 2.524(2) Å between the Cu and O3 indicates weak coordination of nitrate to the Cu atom (Table III). It is interesting that the coordination geometry about the copper(II) ion is a distorted octahedron with a N_4O_2 binding set. In the reported Cu(II) complexes, the Cu(II) is not often in a *pseudo*-O_h environment.

TABLE I Summary of crystal data and refinement results for the $[Cu(cbIm)_4(NO_3)_2]$

Empirical formula	$C_{22}H_{18}Cu_{0.5}N_7O_3$
Formula weight	460.20
Crystal system	Triclinic
Space group	*P*-1
a (Å)	8.249 (2)
b (Å)	8.735 (2)
c (Å)	16.597 (2)
α (°)	81.980 (10)
β (°)	88.540 (10)
γ (°)	63.570 (10)
V (Å^3)	1059.5 (4)
Z	2
T (°C)	25 (2)
D_{calcd} (g cm^{-3})	1.443
F(000)	475
μ(MoKα) (cm^{-1})	5.83
Collection range (°)	$5.26 < 2\theta < 50.00$
Range of *h*, *k*, *l*	$0 \sim 9, -9 \sim 10, -19 \sim 19$
No. of reflections collected	4141
No. of independent reflections	3389 ($R_{int} = 0.0111$)
$R(I > 2\sigma(I))$ on F^2	0.0394
$wR(I > 2\sigma(I))$ on F^2	0.0991
R(all data) on F^2	0.0489
wR(all data) on F^2	0.1027
Goodness-of-fit	1.024
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.449, −0.198

No multinuclear species were detected even in the presence of excess metal ion. The absence of species with coordination of cyano group may be due to two possible reasons. The significant difference of coordination abilities between imidazole and cyano groups results in the coordination of imidazole to copper(II) preferentially. Secondly, the title complex formed by coordination of imidazole to copper(II) is stable enough to prevent further coordination of cyano group to copper(II). The cyano group is not coordinated in the previously reported Cu(II) and Mn(II) complexes with hexaazatriphenylene hexacarbonitrile and 4-cyanopyridine ligands [17,18]. The title complex is stabilized by favorable π–π interactions. The center-to-center distance of 4.13 Å indicates the existence of π–π interactions between the phenyl planes of two adjacent molecules. The nearest intermetallic distance of 8.25 Å implies the absence of any interactions between two adjacent copper atoms which is supported by magnetic measurements.

The crystal packing of the molecules shows hydrogen bonding between C3–H3$\cdots$O1$^{\#1}$ [C3–O1$^{\#1}$ = 3.453(5) Å, C3–H3–O1$^{\#1}$ = 161°], symmetry code: $2-x, 1-y, -z$; C13-H13$\cdots$N3$^{\#2}$ [C13–N3$^{\#2}$ = 3.455 (4) Å, C13–H13–N3$^{\#2}$ = 177°], symmetry code: $2-x, -y, 1-z$; C18–H18$\cdots$N6$^{\#3}$ [C18–N6$^{\#3}$ = 3.411 (5) Å, C18–H18–N6$^{\#3}$ = 154°], symmetry code: $3-x, -2-y, 1-z$ and C20–H20$\cdots$O1$^{\#4}$ [C20-O1$^{\#4}$ = 3.307 (5) Å, C20–H20–O1$^{\#4}$ = 146°], symmetry code: $2-x, -y, -z$.

In order to investigate whether the NO_3 hydrogen bonding is an important structure determining factor, the reactions between the cbIm ligand and other Cu(II) salts were also carried out. Unfortunately, blue precipitates which are insoluble in usual organic solvents appeared when aqueous solutions of the Cu(II) salt, e.g. $Cu(ClO_4)_2 \cdot 6H_2O$, were added to the acetonitrile solution of cbIm. The results suggest that different products were produced by reactions of the cbIm ligand with other Cu(II) salts.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[Cu(cbIm)_4(NO_3)_2]$

	x/a	y/b	z/c	$U_{(eq)}$
Cu	10000	0	0	38.2 (2)
O(1)	4747 (4)	10001 (4)	−1405 (2)	89 (1)
O(2)	5018 (4)	7815 (3)	−574 (2)	93 (1)
O(3)	2809 (3)	10253 (3)	−483 (2)	80 (1)
N(1)	9506 (3)	2252 (2)	397 (1)	39 (1)
N(2)	10085 (3)	3986 (3)	1047 (1)	40 (1)
N(3)	9185 (5)	2131 (4)	5513 (2)	92 (1)
N(4)	11226 (3)	−1218 (2)	1083 (1)	39 (1)
N(5)	13246 (3)	− 2368 (3)	2094 (1)	46 (1)
N(6)	15956 (5)	− 11297 (4)	4155 (2)	89 (1)
N(7)	4164 (3)	9398 (3)	− 827 (2)	51 (1)
C(1)	8017 (4)	3841 (3)	318 (2)	45 (1)
C(2)	8370 (4)	4921 (3)	714 (2)	46 (1)
C(3)	10721 (4)	2410 (3)	824 (2)	42 (1)
C(4)	11018 (4)	4511 (4)	1609 (2)	51 (1)
C(5)	10703 (4)	3997 (3)	2486 (2)	44 (1)
C(6)	9675 (4)	5220 (3)	2971 (2)	51 (1)
C(7)	9325 (4)	4745 (4)	3756 (2)	56 (1)
C(8)	10002 (4)	3026 (4)	4068 (2)	51 (1)
C(9)	11057 (5)	1778 (4)	3596 (2)	64 (1)
C(10)	11417 (5)	2277 (4)	2822 (2)	64 (1)
C(11)	9567 (5)	2512 (4)	4877 (2)	65 (1)
C(12)	10348 (4)	− 1098 (3)	1797 (2)	47 (1)
C(13)	11582 (4)	− 1815 (3)	2428 (2)	52 (1)
C(14)	12968 (4)	− 1992 (3)	1285 (2)	43 (1)
C(15)	14998 (4)	− 3276 (4)	2544 (2)	60 (1)
C(16)	15301 (4)	− 5056 (4)	2924 (2)	50 (1)
C(17)	15006 (5)	− 5383 (4)	3734 (2)	64 (1)
C(18)	15201 (5)	− 6999 (4)	4078 (2)	68 (1)
C(19)	15701 (4)	− 8289 (4)	3602 (2)	54 (1)
C(20)	15990 (5)	− 7981 (4)	2791 (2)	72 (1)
C(21)	15801 (5)	− 6363 (4)	2455 (2)	68 (1)
C(22)	15842 (5)	− 9966 (4)	3929 (2)	68 (1)

TABLE III Selected bond distances (Å) and angles (°) for the complex $[Cu(cbIm)_4(NO_3)_2]$

Cu–N(4)	1.997 (2)	Cu–N(1)	2.026 (2)
(Cu–N)av	2.012 (2)	Cu–O(3)	2.524 (2)
O(3)–Cu–O(3)$^{\#1}$	180.0 (1)	O(3)–Cu–N(1)	81.0 (1)
O(3)–Cu–N(1)$^{\#1}$	99.0 (1)	O(3)–Cu–N(4)	90.8 (1)
O(3)–Cu–N(4)$^{\#1}$	89.2 (1)	N(1)–Cu–N(1)$^{\#1}$	180.0 (1)
N(1)–Cu–N(4)	87.85 (8)	N(1)–Cu–N(4)$^{\#1}$	92.15 (8)
N(4)–Cu–N(4)$^{\#1}$	180.00 (14)		

Symmetry transformations used to generate equivalent atoms:
$^{\#1} 2 - x, -y, -z$.

Magnetic Properties

The magnetic properties for a powder sample of $[Cu(cbIm)_4(NO_3)_2]$ were measured over the temperature range $70 \sim 300$ K. The observed magnetic moment of 2.00 μ_B per molecule at room temperature is close to the spin only value of 1.73 μ_B. The effective moment remains almost unchanged over the measured temperature range for the

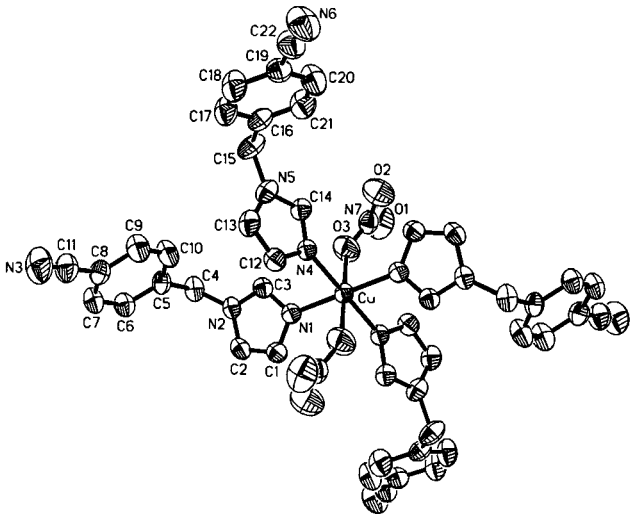

FIGURE 1 The molecular structure of $[Cu(cbIm)_4(NO_3)_2]$ showing 50% probability displacement ellipsoids and atom numbering scheme. Hydrogen atoms have been omitted for clarity.

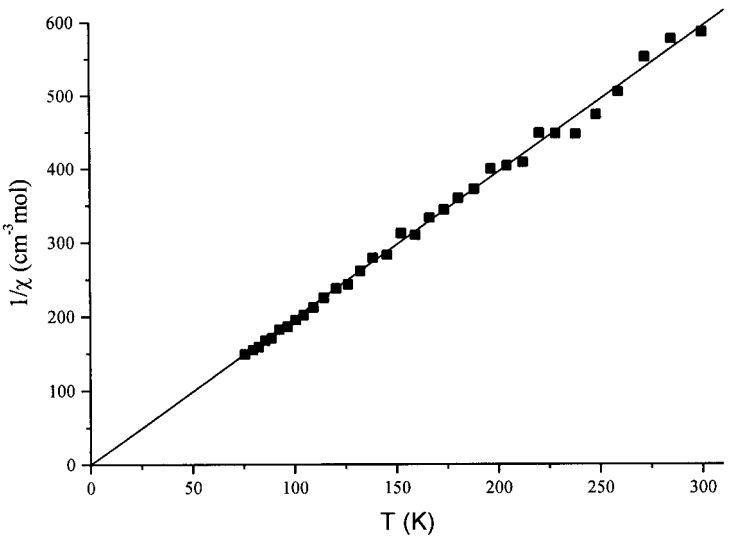

FIGURE 2 Plot of inverse magnetic susceptibility *vs.* temperature for $[Cu(cbIm)_4(NO_3)_2]$.

title compound. Both $1/\chi$ and μ are linearly dependent on temperature. The complex shows Curie behavior as its magnetic susceptibilities are linearly dependent on $1/T$ (Fig. 2) [19]. The results indicate that there is practically no magnetic interaction between the neighboring Cu(II) ions in this mononuclear complex.

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