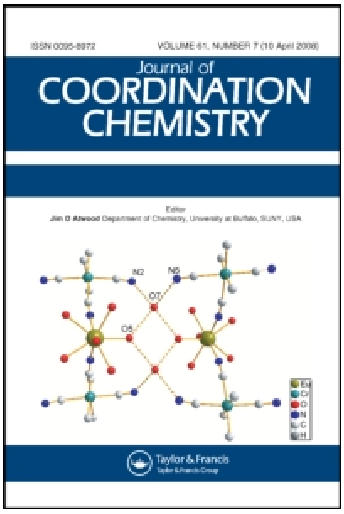

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A new mixed-ligand copper(II) complex containing azide and 1,10-phenanthroline: crystal structure and properties

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A NEW MIXED-LIGAND COPPER(II) COMPLEX CONTAINING AZIDE AND 1,10-PHENANTHROLINE: CRYSTAL STRUCTURE AND PROPERTIES

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A new copper complex, $[Cu(phen)_2N_3]ClO_4$ (phen = 1,10-phenanthroline), has been synthesized and characterized by X-ray single-crystal structure analysis. The copper atom is five-coordinated with four nitrogen atoms of two phens and one nitrogen atom of the azide to form an intermediate coordination geometry distorted from trigonal bipyramidal (TBP) and square pyramidal (SP). The extended three-dimensional structure is formed through π–π interactions and hydrogen bonds. The IR spectrum, electronic spectrum, magnetic properties and ESR spectrum of the title compound have been studied.

Keywords: Copper(II) complex; Hydrogen bond; Phenanthroline; Azide

INTRODUCTION

Five-coordinated complexes of the copper(II) ion have received much attention stereochemically, spectrochemically and biologically, and have been comprehensively discussed [1]. Usually there are two stable geometries for copper(II) complexes with five equal coordination atoms: SP and TBP. Reinen *et al.* studied a series of the complexes of the type $[Cu(terpy)_2X_2]$ and found that SP is the favored geometry when $X = Cl^-$ and NO_2^-, while TBP is the favored geometry when $X = Br^-$ and SCN^- [2]. However, to our knowledge no five-coordinated complex containing both N_3^- and another ligand has previously been structurally characterized. On the other hand, self-assembly of metal compounds by hydrogen bonds into one-, two-, and three-dimensional supramolecular architectures is important in the crystal engineering of nonlinear optical, conducting and ferromagnetic materials [3–6]. Despite this, the

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number of studies dealing with high-dimensionality systems containing both hydrogen bonds and π–π interactions is still rather limited because they are extremely difficult to control. In view of this, we report here the synthesis, structure and spectroscopic properties of the mixed-ligand compound [Cu(phen)$_2$N$_3$]ClO$_4$, in which the three-dimensional network is formed through extended hydrogen bonds and π–π interactions.

EXPERIMENTAL

Preparation of [Cu(phen)$_2$N$_3$]ClO$_4$

Single crystals suitable for X-ray investigations were obtained by a slow diffusion method using an H-shaped tube with an aqueous solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in one arm and a mixture of NaN_3 and phen in the other arm. After a few weeks, green crystals were obtained. The product was washed with ether and dried in vacuum, yield 50%. Anal. Calcd. for $C_{24}H_{16}ClCuN_7O_4$ (%): C, 50.98; H, 2.83; N, 17.33. Found C, 50.62; H, 2.94; N, 17.18.

Physical Measurements

The electronic spectrum was measured with a Jasco-570 spectrophotometer. Infrared spectroscopy on KBr pellets was performed on a Shimadzu IR-408 spectrophotometer in the 4000–400 cm^{-1} region, and the X-band ESR spectrum was obtained on a Bruker ER 200 D-SRC ESR spectrometer.

X-ray Crystallography

Crystal data: $C_{24}H_{16}ClCuN_7O_4$, triclinic, space group P-1, $a = 7.580(2)$, $b = 10.080(3)$, $c = 15.847(5)$ Å; $\alpha = 99.370(5)$, $\beta = 100.899(6)$, $\gamma = 102.049(6)^\circ$, $V = 1136.8(6)$ Å^3, $Z = 2$, $D_{c} = 1.652\,\mathrm{g\,cm^{-3}}$, $T = 293(2)$ K. $R1 = 0.0564$, $wR2 = 0.1235$ [$I > 2\sigma(I)$] and $R1 = 0.1063$, $wR2 = 0.1455$ (all data). Determination of the unit cell and data collection was performed on a Bruker Smart 1000 area detector using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A total of 5894 independent reflections were collected, of which 4430 [$R_{\mathrm{int}} = 0.0310$] reflections were used in the succeeding structure determination and refinement. The structure of the title compound was solved by direct methods and successive Fourier difference syntheses (*SHELXS*-97) and refined by full-matrix least-squares procedure on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (*SHELXL*-97) [7]. Further details of the structural analyses are summarized in Table I.

RESULTS AND DISCUSSION

Crystal Structure

The structural analysis shows that the formula of the complex is [Cu(phen)$_2$N$_3$]ClO$_4$. An ORTEP drawing of the title compound is shown in Fig. 1. Selected bond lengths and angles are given in Table II.

TABLE I Data collection and processing parameters of the title compound

Formula	$C_{24}H_{16}ClCuN_7O_4$
Formula weight	565.43
Crystal system	Triclinic
Space group	$P1$
a (Å)	7.580(2)
b (Å)	10.080(3)
c (Å)	15.847(5)
α (°)	99.370(5)
β (°)	100.899(6)
γ (°)	102.049(6)
V (Å^3)	1136.8(6)
Z	2
D_{calc} (g cm^{-3})	1.652
Crystal size	0.30 × 0.20 × 0.10
F(000)	574
θ Range for data collection	1.34 to 26.42
Reflections measured	5894
Unique reflections	4430
R(int)	0.0310
GOF	1.025
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0564, 0.1235
R1, $wR2$ (all data)	0.1063, 0.1455

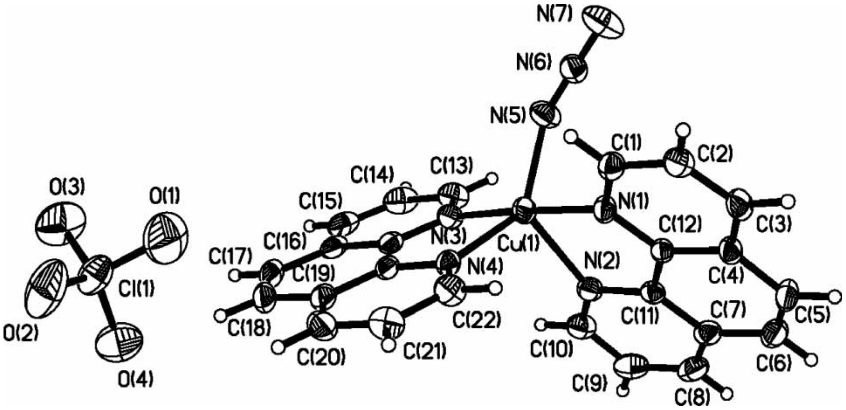

FIGURE 1 ORTEP drawing of $[Cu(phen)_2N_3]ClO_4$ showing the atom labeling scheme.

The copper atom is five coordinated with four nitrogen atoms from two phen ligands and one terminal nitrogen atom from azide to form a CuN_5 coordination environment with an intermediate geometry between flattened TBP and elongated SP. If we view the coordination polyhedron as distorted TBP, N(2), N(4), N(5) build the equatorial plane and N(1), N(3) occupy the axial positions; but from SP geometry, N(1), N(3), N(4), N(5) build the plane and N(2) occupies the apex. The bond lengths and angles show that the coordination geometry around the copper(II) ion deviates markedly from regular TBP and SP, so the actual symmetry should be rationally regarded as C_{2v}. Two phen ligands are bidentately bonded to copper, forming two five-membered chelate rings and resulting in severe steric hindrance. The $Cu–N_{phen}$ bonds [1.996(4), 1.997(4), 2.070(4), 2.149(4) Å] are slightly longer than the $Cu–N_{azide}$ bond [1.984(4) Å]. The dihedral angle of the two phen ligands is 116.9°. The angle

TABLE II Selected bond lengths (Å) and angles (°) for the title compound

Cu(1)–N(5)	1.984(4)
Cu(1)–N(1)	1.996(4)
Cu(1)–N(3)	1.997(4)
Cu(1)–N(4)	2.070(4)
Cu(1)–N(2)	2.149(4)
N(5)–Cu(1)–N(1)	92.89(16)
N(5)–Cu(1)–N(3)	89.68(16)
N(1)–Cu(1)–N(3)	177.11(15)
N(5)–Cu(1)–N(4)	138.71(17)
N(1)–Cu(1)–N(4)	97.66(15)
N(3)–Cu(1)–N(4)	81.23(15)
N(5)–Cu(1)–N(2)	113.86(17)
N(1)–Cu(1)–N(2)	79.97(15)
N(3)–Cu(1)–N(2)	97.78(15)
N(4)–Cu(1)–N(2)	107.27(14)
N(6)–N(5)–Cu(1)	124.2(4)

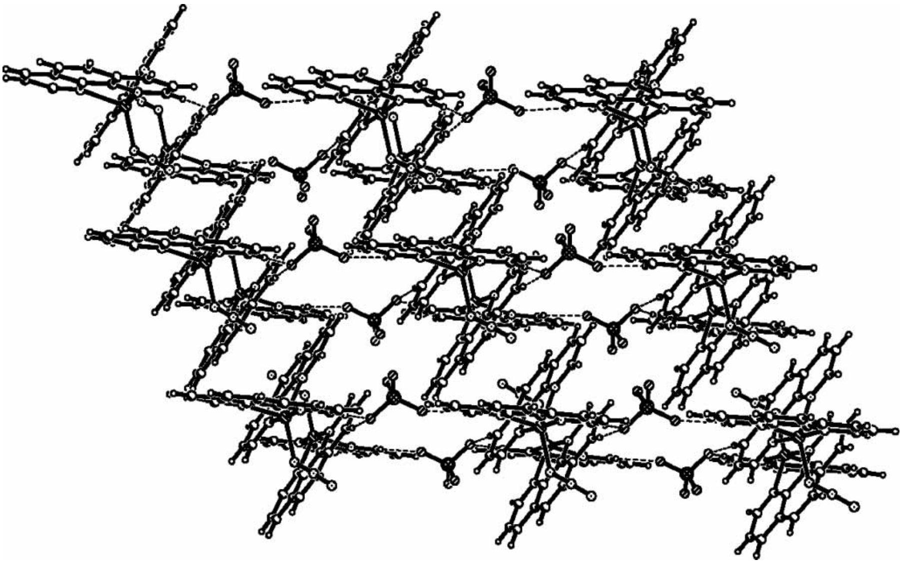

FIGURE 2 View of the self-assembly through hydrogen bonds.

N(1)–Cu(1)–N(3) is nearly linear (177.11°). In addition, extensive intermolecular hydrogen bonds are formed in the crystal through oxygen atoms of the non-coordinated perchlorate anion and the hydrogen atoms of phen ligands as shown in Fig. 2. The interplanar distance between the phen rings of two adjacent molecules is 3.311 Å, indicating definite π-stacking interactions. The π–π interactions between two parallel phen rings of different molecules are shown in Fig. 3. The 3-D network resulting from hydrogen bonds and π–π stacks in the crystals is depicted in Fig. 4.

IR and Electronic Spectra

The IR spectrum of the title complex shows several characteristic absorptions. The strong bond at 2120 cm^{-1} is assigned to $\upsilon(N_3^-)$ of coordinated azide, the medium

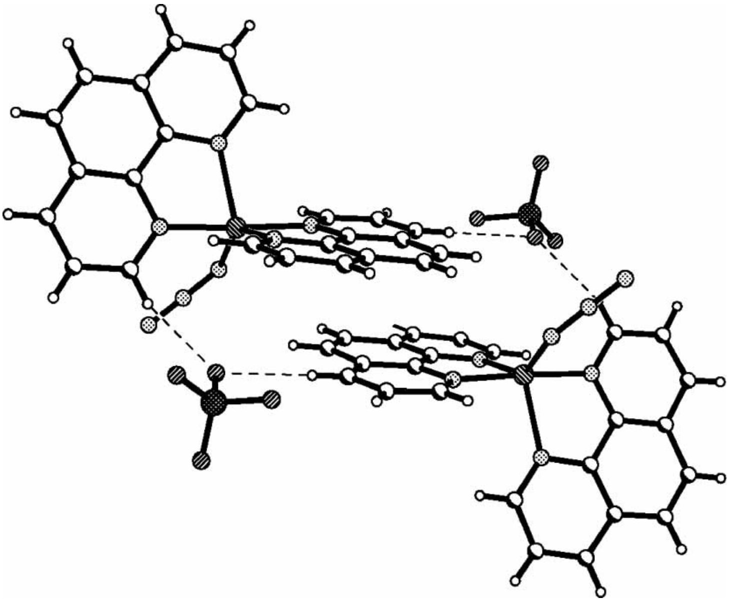

FIGURE 3 The π–π interactions in [Cu(phen)$_2$N$_3$]ClO$_4$.

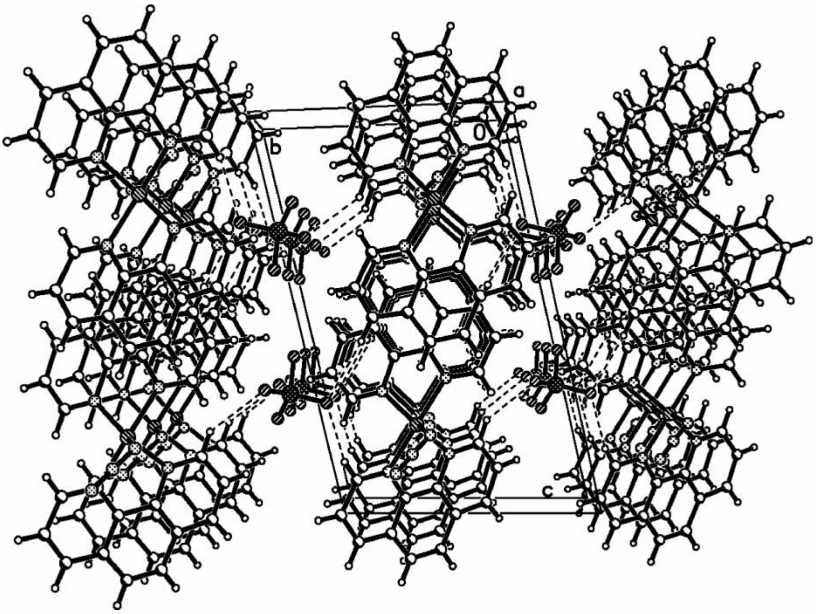

FIGURE 4 The three-dimensional structure of [Cu(phen)$_2$N$_3$]ClO$_4$.

bands at 1620–1510 cm^{-1} are due to υ(C=N) and υ(C=C) stretchings of the coordinated phen molecules. In addition, a broad bond attributed to the ClO$_4^-$ anion at 1100 cm^{-1} was also observed, and the lack of any splitting would be consistent with a non-coordinated tetrahedral ClO$_4^-$. The electronic spectrum of [Cu(phen)$_2$N$_3$]ClO$_4$

in DMF solution at ambient temperature was measured. The bands at $35\,000\,\text{cm}^{-1}$ ($\varepsilon = 9.98 \times 10^3\,\text{L mol}^{-1}\,\text{cm}^{-1}$) and $44\,200\,\text{cm}^{-1}$ ($\varepsilon = 3.5 \times 10^3\,\text{L mol}^{-1}\,\text{cm}^{-1}$) are assigned to π–π transition within ligands. The band at $25200\,\text{cm}^{-1}$ ($\varepsilon = 5.8 \times 10^3\,\text{L mol}^{-1}\,\text{cm}^{-1}$) can be ascribed to metal-to-ligand charge transfer. The broad band in the visible region centered at $15000\,\text{cm}^{-1}$ ($\varepsilon = 478\,\text{L mol}^{-1}\,\text{cm}^{-1}$) with a low extinction coefficient is assigned to d–d transitions of the copper(II) ion. Based on the crystal structure symmetry of the title compound, the symmetry around the copper(II) ion can be regard as C_{2v}, which would theoretically produce three transitions ($^2A_1 \rightarrow$, $^2B_1$, $^2A_2$, $^2B_2$). The absorption observed at $15\,000\,\text{cm}^{-1}$ may incorporate all three transitions owing to their very similar energies.

Magnetic Properties

The effective moment (μ_{eff}) of the complex at room temperature is 1.93 μ_B. This value is slightly higher than the spin-only value of one copper(II) ion (1.73 μ_B) owing to mixing-in of angular momentum from excited states via spin–orbit coupling [8].

ESR Spectrum

The ESR spectrum of $[Cu(phen)_2N_3]ClO_4$ in DMF at 110 K showed an axial pattern. Computer simulation gave the ESR parameters $g_x = 2.03$, $g_y = 2.07$, $g_z = 2.28$ (Fig. 5).

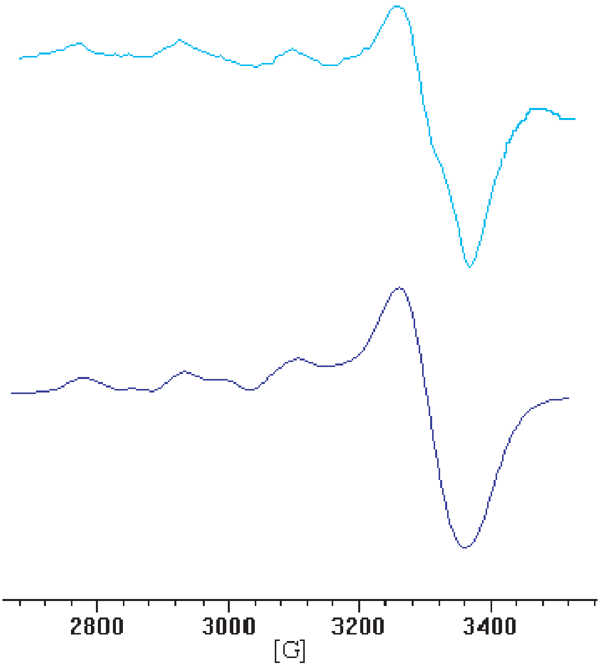

FIGURE 5 ESR spectrum of $[Cu(phen)_2N_3]ClO_4$ in DMF at 110 K (top) and computer simulation spectrum (bottom).

The ground-state wave function of a pentacoordinated copper(II) ion complex with an intermediate geometry between TBP and SP is [2]:

$$\varphi_g = (1 + c^2)^{-1/2}\{\mathrm{d}_{z^2} + c\mathrm{d}_{x^2-y^2}\} \tag{1}$$

where the mixing coefficient c is 0 for TBP (d_{z^2} ground state) and $1/3^{1/2}$ for SP ($\mathrm{d}_{x^2-y^2}$ ground state). When the z axis is defined as parallel to the magnetic field and x, y as perpendicular, the g tensor of the three directions can be described as

$$g_y = g_0 + \frac{8c^2}{1+c^2}u_y \tag{2}$$

$$g_x = g_0 + \frac{2c^2}{1+c^2}\left(1 - \frac{\sqrt{3}}{c}\right)^2 u_x \tag{3}$$

$$g_z = g_0 + \frac{2c^2}{1+c^2}\left(1 + \frac{\sqrt{3}}{c}\right)^2 u_z \tag{4}$$

where g_0 is the value for a free ion (2.0023). The orbital contribution u is defined as

$$u = \frac{k_i^2 \zeta_0}{\Delta E_i} \tag{5}$$

where ΔE_i refers to d–d transition energies, and k_i and ζ_0 ($830\,\mathrm{cm}^{-1}$) are covalency factors and the spin–orbital coupling parameter for the free copper(II) ion, respectively. Theoretically, ΔE_i should be different for g_x, g_y and g_z. Here we use the approximation $\Delta E_x = \Delta E_y = \Delta E_z = 15\,000\,\mathrm{cm}^{-1}$, and, to avoid more parameters, only one k value is considered ($k = k_x = k_y = k_z$). With this transition energy, $k = 0.73$ and $c = 0.4$ can reproduce the best experimental g values. The c value implies that the complex takes on the intermediate geometry and is less distorted from regular TBP ($c = 0$) and considerably distorted from SP ($c = 1/3^{1/2}$), which is consistent with the crystal structure of the complex.

Acknowledgements

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Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 209307. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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