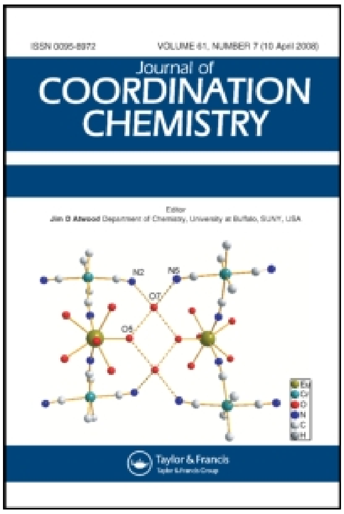

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A mixed-ligand complex containing four- and five-coordinate copper(II)

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A mixed-ligand complex containing four- and five-coordinate copper(II)

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The copper(II) complex $[Cu(L)(en)_2]_2[Cu(en)_2](L)_2(ClO_4)_6$, L = 4-2-pyridine-1,2,4-triazole, en = ethylenediamine has been prepared and characterized. Crystals are triclinic, space group $P\bar{1}$ with $Z=1$, $a=8.637(3)$, $b=13.850(4)$, $c=16.295(5)$ Å, $\alpha=106.662(6)$, $\beta=104.039(6)$, $\gamma=97.616(6)^\circ$, $V=1768.4(10)$ Å^3. The structure of the title compound consists of three independent cations with two five-coordinate $[Cu(L)(en)_2]$ units and a four-coordinated $[Cu(en)_2]$ unit with two weak axial Cu–N interactions to lattice ligand molecules (2.552 Å). Other physical properties are described. Both the ligand and the complex fluoresce with different luminescent process.

Keywords: 4-2-Pyridine-1,2,4-triazole; Ethylenediamine; X-ray structure; Fluorescence

1. Introduction

1,2,4-Triazole and, in particular, its derivatives are of interest as bridging ligands for the preparation of polynuclear metal complexes because they can be coordinated to a metal atom in different ways, depending on the position and the nature of substituents [1]. Transition metal complexes of 1,2,4-triazole derivatives are intriguing from both theoretical and practical viewpoints and are the subject of several magnetic studies [2–5]. Iron(II) complexes of 1,2,4-triazole derivatives exhibit spin-crossover behaviour [6–8]. Complexes of 3,5-substituted 1,2,4-triazoles have been extensively investigated during the last decade [1, 9–12], because of their tendency to form various high-dimensional coordination polymers and interesting magnetic properties.

Recent research is focussed on bis-triazole complexes, which are always self-assembled to form multidimensional structures [13]. Previously, we reported a series of 3,5-substituted triazole coordination polymers of cadmium that are zero- to three-dimensional, depending on different triazole ligands and anions [9]. We also reported the first helical triazole metal complexes [13a], Zn(II) triazole complexes with blue fluorescent properties, and Fe(II) trizole complexes with spin-crossover properties [14]. To further investigate the structures and properties of triazole-based

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complexes, 4-2-pyridine-1,2,4-triazole (L) was used to synthesize a novel complex $[Cu(L)(en)_2]_2[Cu(en)_2](L)_2(ClO_4)_6$ (**1**) (en = ethylenediamine). Results of a study of **1** are reported below.

2. Experimental

The triazole ligand was synthesized according to a literature method [15]. All other reagents were commercially available and used without further purification. C, H, and N microanalyses were carried out with a Perkin-Elmer 240 system analyzer. FT-IR spectra (KBr pellets) were recorded in the range 400–4000 cm^{-1} on a Bio-Rad FTS 135 spectrophotometer and electronic spectra (aqueous solution) on a Shimadju U-2001 spectrophotometer. X-band EPR spectra of crystalline samples were recorded on a Bruker ER 200 D-SRC spectrometer. The photoluminescence spectra were measured with an MPF-4 spectrophotometer with a xenon arc lamp as the light source.

2.1. *Preparation of $[Cu(L)(en)_2]_2[Cu(en)_2](L)_2(ClO_4)_6$ (1)*

A solution of L (0.4 mmol) in boiling water (15 cm^3) was added into an aqueous solution (3 cm^3) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.2 mmol) with stirring. The mixture was filtered into an aqueous solution containing en (2 mmol). Crystals of **1** suitable for X-ray diffraction were obtained by evaporation of the filtrate during one week. Yield: 24%. Anal. Calcd for $C_{40}H_{72}Cl_6Cu_3N_{28}O_{24}$ (%): C, 27.73; H, 4.18; N, 22.64%. Found: C, 27.80; H, 4.22; N, 22.72. IR: 3350vs, 3295vs, 3100vs, 2946m, 2851m, 1610m, 1577s, 1482m, 1151vs, 1131vs, 1115vs, 1082s, 823m, 663s, 515m cm^{-1}.

2.2. *X-ray crystallography*

Diffraction intensities were collected on a Bruker SMART 1000 CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the ω-scan technique. Lorentz polarization and absorption corrections were applied. The structure was solved by direct methods and refined with full-matrix least-squares techniques using SHELXS-97 and SHELXL-97 [16]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Analytical expressions of neutral-atom scattering factors were employed and anomalous dispersion corrections were incorporated. Crystallographic data and selected bond lengths are listed in tables 1 and 2, respectively.

3. Results and discussion

The structure of **1** consists of two $[Cu(en)_2(L)]$ units, a $[Cu(en)_2]$ unit and two free L ligands as shown in figure 1. Each copper(II) ion is coordinated via two en molecules to form a nearly planar configuration, with L ligands in axial positions. In the square-based pyramidal $[Cu(en)_2(L_1)]$ units, the Cu–N bond length in the axial direction

Table 1. Crystallographic data and refinement details for **1**.

Empirical formula	$C_{40}H_{72}Cl_6Cu_3N_{28}O_{24}$
Formula weight	1732.58
Crystal system	Monoclinic
Space group	$P\bar{1}$
T (K)	293(2)
a (Å)	8.637(3)
b (Å)	13.850(4)
c (Å)	16.295(5)
α (°)	106.662(6)
β (°)	104.039(6)
γ (°)	97.616(6)
V (Å^3)	1768.4(10)
Z	1
F(000)	889
ρ (Mg m^{-3})	1.627
GOF	1.007
R_1 ($I > 2\sigma(I)$)	0.0521
wR_2 ($I > 2\sigma(I)$)	0.1068
R_1 (all data)	0.1120
wR_2 (all data)	0.1349

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Cu(1)–N(1)	2.019(4)	Cu(1)–N(4)	2.022(4)
Cu(1)–N(2)	2.032(4)	Cu(1)–N(5)	2.234(4)
Cu(2)–N(10)	2.011(4)	Cu(2)–N(10)#1	2.011(4)
N(1)–Cu(1)–N(4)	95.01(16)	N(1)–Cu(1)–N(3)	170.42(17)
N(1)–Cu(1)–N(2)	83.49(17)	N(4)–Cu(1)–N(2)	161.36(16)
N(1)–Cu(1)–N(5)	94.54(18)	N(4)–Cu(1)–N(5)	94.59(16)
N(2)–Cu(1)–N(5)	104.05(15)	N(10)–Cu(2)–N(9)	84.84(17)
N(10)–Cu(2)–N(9)#1	95.16(17)	N(9)#1–Cu(2)–N(9)	180.000(1)
Cu(1)–N(3)	2.022(4)	N(3)–Cu(1)–N(2)	94.21(16)
Cu(2)–N(9)	2.014(4)	N(3)–Cu(1)–N(5)	95.04(15)
Cu(2)–N(9)#1	2.014(4)	N(10)#1–Cu(2)–N(9)	95.16(17)
N(4)–Cu(1)–N(3)	84.20(16)		

Symmetry transformation used to generate equivalent atoms is #1: $-x+2$, $-y+1$, $-z+1$.

(2.234 Å) is significantly longer than that between Cu(II) and en molecules. The copper ions in the [Cu(en)$_2$] unit are weakly linked two N1 atoms of two free L ligands (2.552 Å), with what can be described as a 4 + 2 geometry. The dihedral angle between triazole and pyridine rings for coordinated L_1 is 29.1°, while for the free ligand the dihedral angle between the trizole and pyridine rings is 8.4°. Space between Cu(II) cations is filled by perchlorate anions as shown in figure 2.

Electronic spectra of **1** and the free ligand L were recorded in aqueous solution. In the region 200–330 nm, L and **1** show a major band centred at 238 nm, assigned to ligand transitions. Broard absorption by **1** centred at 365 nm can be assigned to ligand to metal charge transfer. In the region 400 to 800 nm, strong absorption peak at 578 nm is attributed to d–d transitions. The electronic spectra could not distinguish four- and five-coordinate copper(II), suggesting that the solution structure of complex **1** is be different to that in the solid state. EPR spectra of **1** as a powder phase, in DMF solution and in frozen DMF solution were recorded. For the powder at room temperature in the $g \approx 2$ region, a strong axial signal with $g_{\parallel} = 2.16$ and $g_{\perp} = 2.06$ typical of square planar

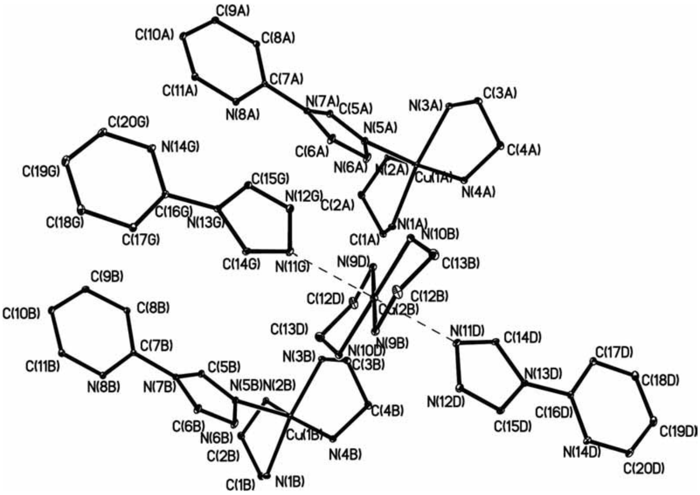

Figure 1. Perspective view of four- and five-coordinate copper(II) in **1** showing the atom numbering scheme.

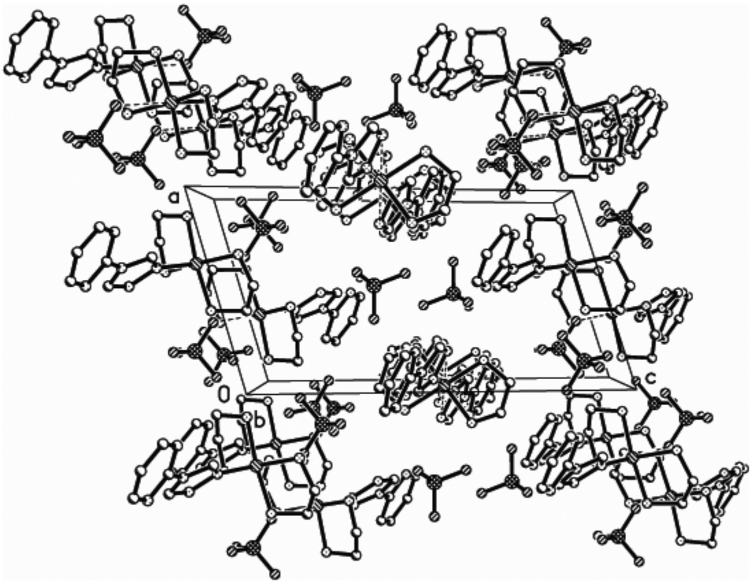

Figure 2. Perspective view of the packing of the structure in **1**.

or square pyramidal copper(II) is observed [18]. No significant difference in the spectrum is found with cooling to liquid nitrogen temperature. EPR spectra of the complex dissolved in DMF solutions at 77 K and room temperature show changes in overall shape, which again suggests that the structure of the title compound in solution is different to that in the solid state.

Luminescent properties of **1** and L have been studied. At ambient temperatures, the free ligand L and **1** in aqueous solution show broad emission maxima at 368 nm and 413 nm with excitation at 308 nm and 334 nm, respectively. For L, the chromophores are the aromatic rings and observed emission is due to a π–π* transition. For **1**, emission can be attributed to charge transfer between metal and ligand, since free L does not luminescence in the range 400–500 nm [17]. It is noted that the emission intensity of **1** is significantly lower than that of the free ligand, which may be due to a different luminescent process.

Supplementary material

Additional crystallographic data are available from CCDC, deposition number 188069. Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk).

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