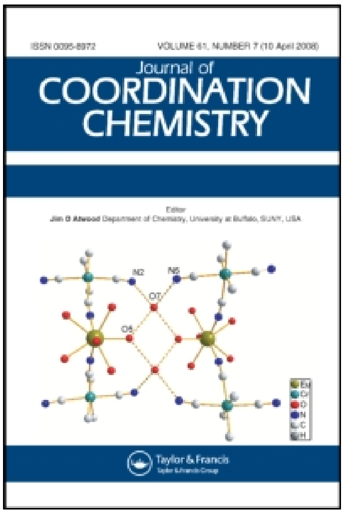

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Synthesis, crystal structure and magnetism of a one-dimensional Cu(II) coordination polymer with monodeprotonated 2,2′-bypyridine-3,3′-diol as bridging ligand

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A new one-dimensional copper(II) coordination polymer, $[Cu(\mu\text{-}HL)(H_2O)_2(NO_3)]_n$ (HL = monodeprotonated 2,2′-bypyridine-3,3′-diol), was synthesized and its crystal structure determined by X-ray crystallography. In the crystal Cu(II) is located a distorted octahedral coordination geometry and each HL coordinates two Cu(II) ions with its two N atoms and an O atom of deprotonated hydroxyl, giving a one-dimensional chain. The variable-temperature (2–300 K) magnetic measurements, analyzed using a one-dimensional Cu(II) magnetic interaction formula, indicate the existence of very weak ferromagnetic coupling with $2J = 0.014\,\mathrm{cm}^{-1}$.

Keywords: Magnetism; Copper(II) complex; Crystal structure; 2,2′-Bipyridine ligand

1. Introduction

Molecular magnetism has attracted considerable attention with major advances in theoretical description and application as new molecular-based materials [1–4], but structure-magnetic relationships remain obscure to reveal and it is necessary to synthesize a large number of complexes with different bridging ligands and study their magnetic properties between structures and magnetism.

2,2′-Bipyridine-3,3′-diol should be a useful bridge because its two N atoms and one or two O atoms from hydroxyl groups may take part in coordination. Complexes with 2,2′-bipyridine-3,3′-diol as ligand have been reported, $[Ru(bpy)_2(HL)]X$ (bpy = 2,2′-bipyridine; X = BPh_4, PF_6) [5], $[Ce(H_2L)(NO_3)_3(H_2O)_2]$ [6], $[Co(HL)_3]\cdot H_2O$ [7], $[Co(HL)_3]\cdot$(1,2-dibromobenzene) [7], $[Cu(HL)_2(H_2O)]$ [8]; binuclear $\{[Ru(\mu\text{-}HL)(bpy)_2]PF_6\}$ [5] and one-dimensional chain coordination polymers $[Cu(\mu\text{-}HL)Cl]_n$ [7], $[Cu(\mu\text{-}HL)Br]_n$ [7], $[Cu(\mu\text{-}HL)(NO_3)]_n$ [7]. These examples deal with the spectroscopy, electrochemistry and porosity, but not magnetism. Interest in magnetic coupling for complexes with 2,2′-bipyridine-3,3′-diol as bridging ligand led to synthesis of the title complex; we report its synthesis, crystal structure and magnetic coupling.

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2. Experimental

2.1. *General*

2,2′-Bipyridine-3,3′-diol was prepared according to the literature method [9]; other chemicals are analytical grade and used without further purification. Infrared spectra were recorded with a Bruker Tensor 27 infrared spectrometer in the 4000–500 cm^{-1} region using KBr discs. C, H and N elemental analyses were carried out on a Perkin–Elmer 240 instrument. Variable-temperature magnetic susceptibilities of microcrystalline powder samples were measured in a magnetic field of 2 KOe in the temperature range 2–300 K on a MPMS-7SQUID magnetometer. The data were corrected for magnetization of the sample holder and for diamagnetic contributions estimated from Pascal's constants.

2.2. *Preparation of [Cu(μ-HL)(H$_2$O)$_2$(NO$_3$)]$_n$*

15 mL hot ethanol solution of 2,2′-bipyridine-3,3′-diol (0.1420 g, 0.755 mmol) was added to 15 mL H_2O solution containing $Cu(NO_3)_2 \cdot 3H_2O$ (0.3642 g, 1.51 mmol) and the mixed solution was stirred for a few minutes. Dilute NaOH solution was added until little precipitate appeared. Green single crystals were obtained after allowing the filtrate to stand at room temperature for two weeks. Anal. Calcd (%), $C_{10}H_{11}CuN_3O_7$: C, 34.44; H, 3.18; N, 12.05; Cu, 18.22. Found (%): C, 34.72; H, 3.38; N, 11.86; Cu, 18.91. IR (cm^{-1}): 1629 m, 1580 m, 1503 w, 1443 s, 1384 s, 1317 s, 1298 s, 1215 m, 1109 w.

2.3. *Crystal structure determination*

A suitable single crystal with dimensions $0.38 \times 0.35 \times 0.28\,\mathrm{mm}^3$ was selected and glued on the tip of a glass fiber. The crystal structure determination was carried out at 25°C on a Bruker Smart-1000 CCD X-ray diffractometer using graphite-monochromatic MoKα radiation ($\lambda = 0.71073$ Å) in the range $4.56 < 2\theta < 51.34°$. A total of 6309 reflections were collected, of which 1864 were independent ($R_{\mathrm{int}} = 0.046$) and 1775 observed reflections with $I > 2\sigma(I)$ were used in the structure analysis. Corrections for Lp factors were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms from water were located in a difference Fourier map and refined as riding in their as-found positions; other hydrogen atoms were placed in the calculated positions and refined as riding. The programs for structure solution and refinement were SHELXTL (Bruker, 2001) [10]. A summary of the crystallographic data is given in table 1.

3. Results and discussion

3.1. *Crystal structure*

Figure 1 shows that Cu1 atom is coordinated by N1, N2, O1, O4, O5 and O7A atoms, in which N1 and N2 atoms are from HL and O7A atom comes from another HL,

Table 1. Crystallographic data.

Formula	$C_{10}H_{11}CuN_3O_7$
Formula weight	348.76
Temperature (K)	298(2)
Crystal system	Orthorhombic
Space group	$Pca2_1$
Unit cell dimensions (Å)	
a	9.790(5)
b	8.943(4)
c	13.975(7)
Volume (Z)	1223.5(10) Å^3, 4
Calculated density (mg m^{-3})	1.893
Absorption coefficient (mm^{-1})	1.827
$F(000)$	708
Crystal size (mm^3)	$0.38 \times 0.35 \times 0.28$
θ range for data collection (°)	2.28–25.67
Limiting indices	$-11 \le h \le 11$, $-10 \le l \le 10$, $-11 \le k \le 16$
Reflections collected	6309
Independent reflection	1864
Data/restraints/parameters	1864/1/190
Goodness-of-fit on F^2	1.046
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0409$, $wR_2 = 0.1046$
R indices (all data)	$R_1 = 0.0429$, $wR_2 = 0.1066$
Largest diff. peak and hole (e/Å^3)	0.324 and −0.317

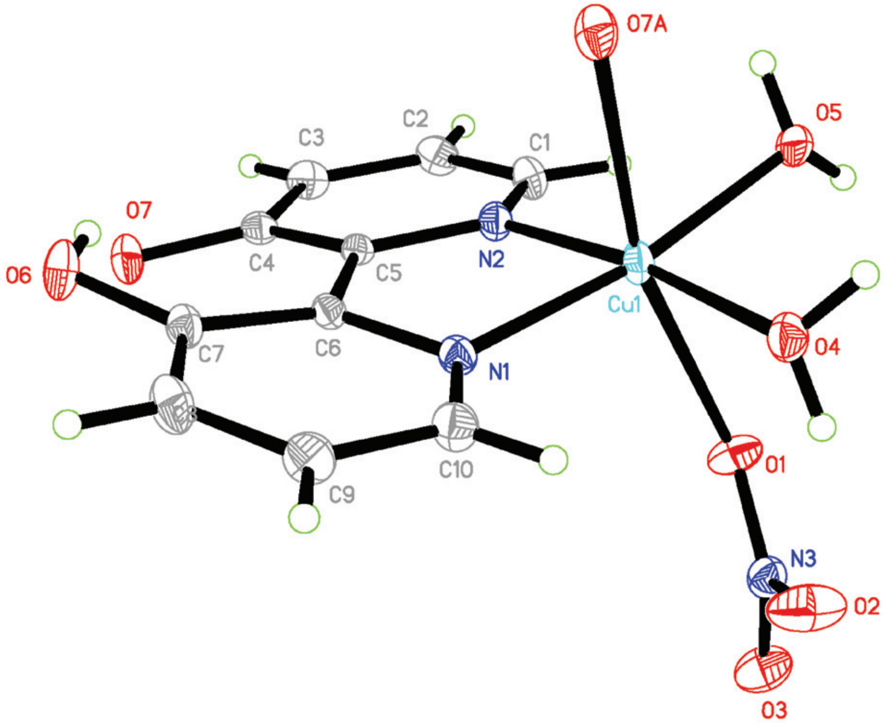

Figure 1. Coordination diagram of the complex with atom numbering scheme.

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

Cu1–O1	2.496(4)	Cu1–O4	2.016(4)	Cu1–O5	1.951(4)
Cu1–O7A	2.440(4)	Cu1–N1	2.006(5)	Cu1–N2	1.956(5)
O5–Cu1–N2	98.11(18)	O5–Cu1–N1	170.4(2)	O5–Cu1–O4	88.62(16)
O5–Cu1–O7A	82.92(15)	O5–Cu1–O1	86.06(15)	N2–Cu1–N1	81.7(2)
N2–Cu1–O4	172.04(18)	N2–Cu1–O7A	97.61(17)	N2–Cu1–O1	91.62(16)
N1–Cu1–O4	92.42(19)	N1–Cu1–O7A	87.61(17)	N1–Cu1–O1	103.52(18)
O4–Cu1–O7A	87.41(15)	O4–Cu1–O1	84.55(15)	O1–Cu1–O7A	166.51(13)

Symmetry code: O7A: $-1/2+x$, $-y$, z.

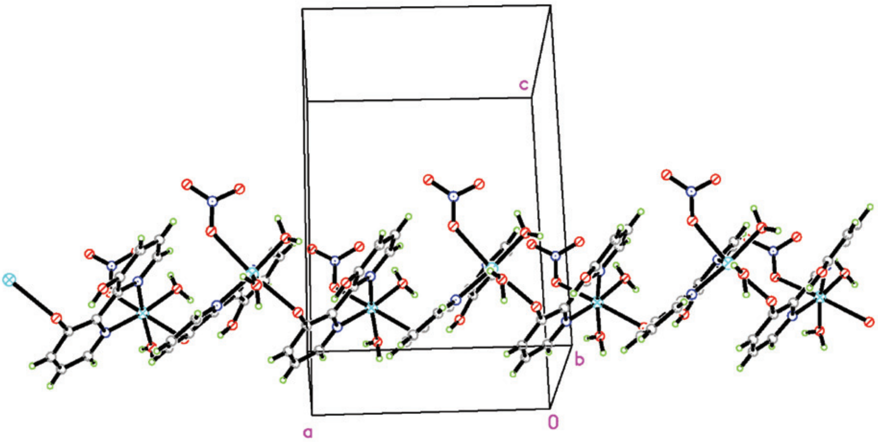

Figure 2. Unit cell and one-dimensional chain structure.

O1 from nitrate anion, and O4 and O5 from two H_2O molecules. The data from table 2 indicate that Cu1 is a distorted octahedral geometry. Figure 1 also indicates that HL is a bridge with its O7 atom coordinated to another Cu(II); each HL connects two Cu(II) ions with separation of 6.838(2) Å resulting in a one-dimensional chain along the *a* axis, as shown in figure 2. In the chain there are O6–H4 $\cdots$ O7 and O4–H8 $\cdots$ O2 hydrogen bonds, and there are inter-chain hydrogen bonds, shown in figure 3 and table 3. The interchain hydrogen bonds form the supermolecular three-dimensional structure. In addition, in the chain there are π–π stacking interactions $\mathrm{Cg1} \cdots \mathrm{Cg2}^{\mathrm{i}} = 3.566(4)$ Å and $\mathrm{Cg1} \cdots \mathrm{Cg2}^{\mathrm{i}}_{\mathrm{perp}} = 3.445$ Å [symmetry codes: (i) $-1/2+X$, $-Y$, Z; Cg1 and Cg2 are the centroids of the N1/C6-C10 ring and N2/C1–C5 ring, respectively; $\mathrm{Cg1} \cdots \mathrm{Cg2}^{\mathrm{i}}_{\mathrm{perp}}$ is the perpendicular distance from Cg1 ring to $\mathrm{Cg2}^{\mathrm{i}}$ ring].

3.2. *Magnetic property*

The variable-temperature (2–300 K) magnetic susceptibilities are shown in figure 4, where χ_M is the molar magnetic susceptibility per mononuclear Cu(II) unit and μ_{eff} is the magnetic moment per Cu(II) ion. The μ_{eff} value at 300 K is 1.88 BM, slightly larger than that of isolated mononuclear Cu(II) (1.73 BM for $g_{\mathrm{av}}=2$) at room temperature; μ_{eff} values increase very slowly with temperature drop and reach a maximum of 1.98 BM at 2.00 K, implying a ferromagnetic exchange between

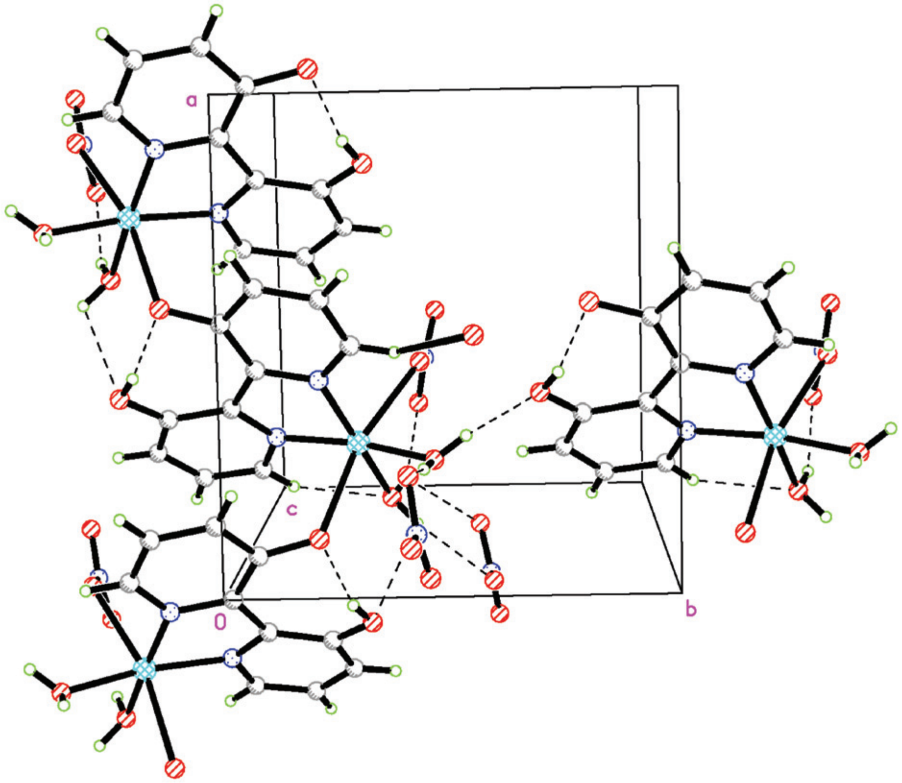

Figure 3. Unit cell and hydrogen bonds.

Table 3. Hydrogen bond lengths (Å) and angles (°).

D–H ··· A	D–H	D ··· H	D ··· A	∠DHA
O6–H4 ··· O7	0.82	1.67	2.400(6)	147
O4–H8 ··· O2	0.85	1.98	2.743(7)	150
O4–H8 ··· O3^{i}	0.85	2.43	2.949(7)	120
O4–H9 ··· O1^{i}	0.85	2.21	2.934(6)	143
O4–H9 ··· O6^{ii}	0.85	2.58	3.055(6)	117
O5–H10 ··· O6^{iii}	0.85	1.82	2.670(5)	172
O5–H11 ··· O2^{iv}	0.84	1.93	2.767(7)	169
C1–H1 ··· O3^{v}	0.93	2.47	3.179(8)	133
C10–H7 ··· O4	0.93	2.43	2.974(7)	117

Symmetry codes: (i) $-1/2+x$, $1-y$, z; (ii) $-1/2+x$, $-y$, z; (iii) x, $1+y$, z; (iv) $1/2-x$, y, $-1/2+z$; (v) $1-x$, $1-y$, $-1/2+z$.

bridged Cu(II) ions. The one-dimensional chain equation (2) was used to fit for the experimental susceptibilities data [11], which was obtained based on an isotropic Hamiltonian operator as presented in equation (1).

$$\widehat{H} = -2\sum J\widehat{S}_{Cu\,i}\widehat{S}_{Cu\,i+1} \tag{1}$$

$$\chi_{\text{chain}} = \frac{\mathrm{N}g^2\beta^2}{4kT}\,(N/D)^{2/3} \tag{2}$$

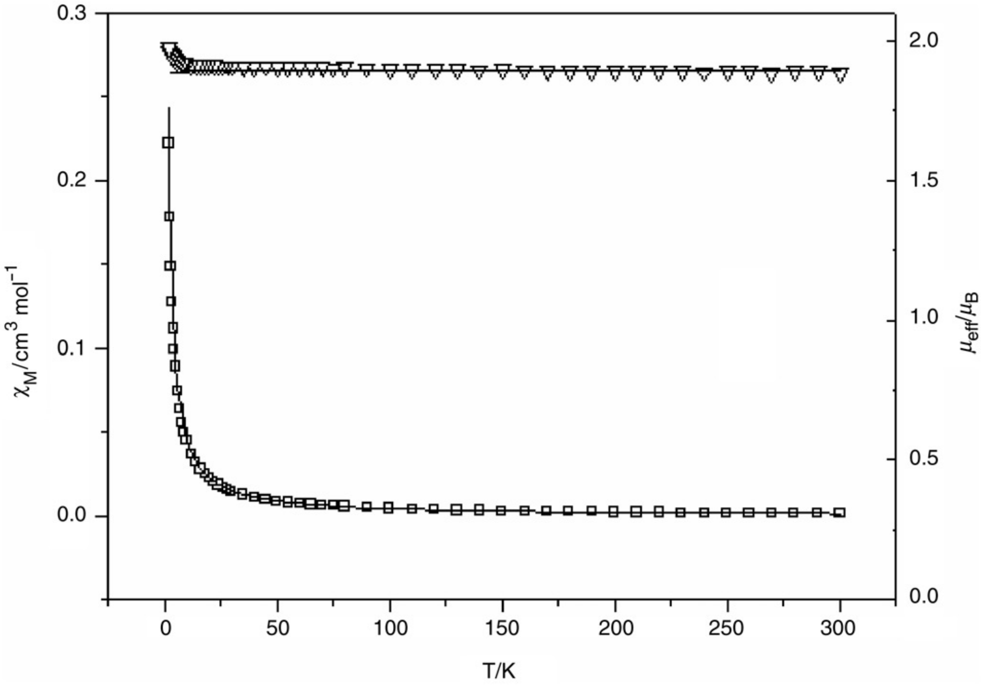

Figure 4. Plots of χ_M (open squares for experimental data, line for theoretical value) and μ_{eff} (down triangle for experimental data, line for theoretical value) *vs.* T for the complex.

$$N = 1.0 + 5.7979916y + 16.902653y^2 + 29.376885y^3 + 29.832959y^4 + 14.036918y^5 \quad (3)$$

$$D = 1.0 + 2.797916y + 7.0086780y^2 + 8.6538644y^3 + 4.5743114y^4 \quad (4)$$

$$y = \frac{J}{2kT} \quad (5)$$

$$\chi = \frac{\chi_{\mathrm{chain}}}{\left(1 - (zJ'/\mathrm{Ng}^2\beta^2)\chi_{\mathrm{chain}}\right)} \quad (6)$$

The theoretical model gave a good fit of the experimental data, with $R = 4.95 \times 10^{-3}$ $[R = \Sigma(\chi_{\mathrm{obsd}} - \chi_{\mathrm{calcd}})^2/(\chi_{\mathrm{obsd}})^2]$, $g = 2.19$, $2J = 0.014\,\mathrm{cm}^{-1}$, $zJ' = 0.00043\,\mathrm{cm}^{-1}$. The value of $2J = 0.014\,\mathrm{cm}^{-1}$ indicates very weak ferromagnetic magnetic coupling between the bridged binuclear Cu(II) ions, and also implies that monodeprotonated 2,2′-bypyridine-3,3′-diol is a bridge ligand that only gives weak magnetic interaction. Weak ferromagnetic coupling between chains is indicated by $zJ' = 0.00043\,\mathrm{cm}^{-1}$.

4. Conclusion

A new one-dimensional chain polynuclear Cu(II) complex has been synthesized with monodeprotonated 2,2′-bypyridine-3,3′-diol as bridging ligands. Fitting of the experimental variable-temperature (2–300 K) magnetic susceptibilities reveals a very weak ferromagnetic coupling between the bridged Cu(II) ions suggesting that monodeprotonated 2,2′-bypyridine-3,3′-diol gives only weak magnetic coupling.

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