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Supramolecular Structure, Thermal and Spectroscopic Properties of a New Coordination Polymer: Catena-Bis(μ_2-4,4′-dipyridyldisulfide-κ^2N,N′)-Bis(AQUO)-Copper(II)di-trifluoromethanesulfonate

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A new supramolecular network of copper (II), [{Cu(bpds)$_2$(H$_2$O)$_2$}]·2CF$_3$SO$_3$]$_n$, (I), (bpds = 4,4′-bipyridildisulfide) has been synthesized and characterized by elemental analysis and Fourier transform infrared (FT-IR) and its structure determined using X-ray crystallography. The thermal decomposition mechanism of the complex was studied by using thermogravimetry-derivative thermogravimetry (TG-DTG) techniques. X-ray structural analysis revealed that the coordination polymer displays 1D chains. The octahedral O$_2$N$_4$ chromophore surrounding the metal ion forms via two trans located water oxygen and four nitrogen from four bpds ligand. The structure consists of Cu(H$_2$O)$_2$ fragments linked by pairs of bpds ligand to form a double-stranded chain. The thermogravimetric analysis indicates sequential loss of adsorbed and coordinated water and triflate counter ion, prior to more comprehensive ligand fragmentation at elevated temperatures.

Keywords Coordination polymers; crystal structure; thermal analysis

Introduction

The design and synthesis of metal–organic frameworks have received considerable interest owing to their potential application [1] as functional material. The genesis of their formation is the combination of polydentate ligands with d-block transition

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elements [2]. The structure and the properties of such materials depend on several factors, i.e., reaction condition [3], metal ion coordination geometry, coordinating ability of the ligand [2c–4], metal–ligand ratio [5], solvent used [6], and weak interactions (H-bonding [7], π-π [8,9], van der Waals [10]. In addition to these factors, the counter ion used, whether coordinating or not, may also play a major role to ultimately control the network [11]. The ligands having two 4-pyridyl donors, e.g., 4,4′-bipyridine [12], bis(4-pyridyl)ethane [6a], 1,4-bis(4-pyridyl)benzene [13], and 4,4′-azo bis(pyridine) [14] have been intensively employed for the construction of several coordination polymers with a wide variety of network topologies and structural motifs, e.g., diamondoid [15], NbO [16] and α-polonium-type [17], ladder [18], square and rectangular grid [19], or composite solids [20]. The 4,4′-bipyridyl disulfide (bpds) [21] is a lesser extend ligand that has a characteristic 90° bent structure and accompanying axial chirality, generating the P and M-forms of enantiomeric [22–23b]. Indeed, this ligand has been frequently used in supramolecular construction and has produced a variety of diverse self-assembled structures upon complexation with various metal ions [24,25]. Hong *et al*. reported two Cu–bpds networks with sulfate and nitrate anions [25]. The study shows that sulfate functions as bridging ligand leading to a 2D architecture, whereas nitrate does not participate in any way in coordination and a double-stranded chain is formed. However, bulkier and chelating coordinating anions, such as hexafluoroacetylacetonate [22–26], malate [23a], acetate, benzoate, and hexanoate [23b], lead to polymers with single bridging bpds ligand. This contribution has as goal reports the synthesis, crystal structure, thermal and spectroscopic properties of a new Cu(II)-bpds derivative with trifluoromethanesulfonate (triflate), as bulkier and chelating coordinating anion. One of the interests in building of this coordination polymer is the creation of a new tuneable functional material with potential applications in gas storage, anion exchange, catalysis, conductivity, luminescence and magnetism.

Experimental

A solution of $Cu(CF_3SO_3)_2$ (36 mg, 0.1 mmol) in water was slowly added to a solution of 4,4′-dipyridyl disulfide (44 mg, 0.2 mmol) in dichloro methane (4 ml). Deep blue single crystals suitable for X-ray were obtained after a few days. Yield: 56%. Anal. Calc. for $C_{22}H_{20}S_6O_8N_4F_6Cu$ (837.23): C, 31.56; H, 2.41; N, 6.69%. Found: C, 31.14, H, 2.63, N, 6.37%. The infrared spectra (KBr pellet) exhibited characteristic dpds ligand bands at 1592, 1487, 1224, 815 and 719 cm^{-1}. The solid complex showed IR spectral bands characteristic for coordinated water at 3400–3500 and 1288–1251 cm^{-1} for the triflate counter ions respectively. Diffraction data were collected at room temperature using a Bruker-Nonius KappaCCD diffractometer with graphite monochromated Mo-Ka radiation ($\lambda = 0.71073$ Å). Frames were collected with the COLLECT program, indexed and processed using Denzo SMN and the files scaled together using the HKL2000 program [27]. Relevant crystal data, experimental conditions and the final refined parameters are listed in Table 1. The absorption correction was applied using a semi-empirical method based on multiple scanned reflections on PLATON [28] program. The structure solution and refinement process was made using the SIR95 [29] and SHELXL-97 [30] programs, respectively. All non-hydrogen atoms were refined with anisotropic thermal parameters using full-matrix least squares procedures on F^2. Hydrogen atoms were located geometrically and refined allowing to ride on their parent atoms with

Table 1. Structure determination summary for $C_{22}H_{20}CuF_6N_4O_8S_6$

Empirical formula	C_{22} H_{20} Cu F_6 N_4 O_8 S_6
Formula weight	838.32 Dalton
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 10.357(3) Å $\alpha = 90°$ b = 11.245(2) Å $\beta = 94.200(9)°$ c = 27.541(8) Å $\gamma = 90°$
Exptl. crystal description	Block
Exptl. crystal colour	Deep Blue
Volume	3199.1(15) $Å^3$
Z	4
Density (calculated)	1.741 Mg/m^3
Absorption coefficient	1.161 mm^{-1}
F(000)	1692
Crystal size	0.22 × 0.10 × 0.08 mm
Theta range for data collection	1.96 to 27.55°
Index ranges	$-13 <= h <= 10$; $-13 <= k <= 8$; $-24 <= l <= 35$
Diffrn. measurement device type	Nonius KappaCCD area-detector diffractometer
Diffrn. measurement method	$\omega/2\theta$
Reflections collected	6438
Independent reflections	4109 [R(int) = 0.0503]
Reflections observed ($>2\sigma$(I))	2496
Data Completeness	0.557
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4109/0/426
Goodness-of-fit on F^2	1.164
Final R indices [$I > 2\sigma$(I)]	R1 = 0.0932 wR2 = 0.1994
R indices (all data)	R1 = 0.1659 wR2 = 0.2432
Largest diff. peak and hole	0.428 and −0.314 e $Å^{-3}$
Computing structure solution	SIR95
Computing structure refinement	SHELXL-97
Refine ls. Hydrogen treatment	Treated by constrained refinement

R indices;
$R_1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$ (based on F),
$wR_2 = [[\Sigma_w(|(F_o^2 - F_c^2|)^2]/[\Sigma_w(F_o^2)^2]]^{1/2}$ (based on F^2).
$w = 1/[(\sigma F_o)^2 + (0.1011^*P)^2 + 4.10^*P]$, where $P = [\max(F_o^2, 0) + 2^*F_c^2]/3$.
Goodness-of-fit $= [\Sigma_w(F_o^2 - F_c^2)^2/(\text{Nobs-Nparameters})]^{1/2}$.

$U_{iso}(H) = 1.2U_{eq}(C)$. FT-IR was recorded on a Nicolet Avatar 330 spectrophotometer using KBr pellets. Elemental analysis (C, H, N) was performed on a Carlo Erba EA 1108 instrument. Dynamic thermogravimetric measurements were

performed using a Mettler TG/SDTA 851[e] thermobalance. The thermogravimetric results were processed by Mettler calorimetric system using the Start[e] program system. Samples were heated in Al_2O_3 pans. Measurements were carried out between 20°C and 800°C at 10° min^{-1} under N_2. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-747001. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk)

Results and Discussion

In the crystal structure of the title compound, (I), is shown in Figure 1 and it crystallizes as deep blue block. The metal, has a distorted octahedral environment, being surrounded by four nitrogen donors from four bpds ligands in the equatorial plane, and by two oxygen atoms from two coordinated water molecules occupying the axial position. The Cu−N bond lengths ranging from 2.020(10)–2.036(8) Å and the Cu−O distances bond are 2.502(9) and 2.466(8) Å. The trans N2−Cu1−N3 and N1−Cu1−N4^{i} bond angles are 174.7(4) and 171.7(4)° and the cis N−Cu−N bond angles are a close range from 89.7(4) to 91.8(3)° and fall in the range of those reported for similar coordination polymers [46–48]. The gauche conformation of the bpds spacer is indicated by C−S−S−C torsion angles of 96.3(6)°, that falls in the range of 83.8(6)–95.5(8)°, found in a series of coordination polymers containing

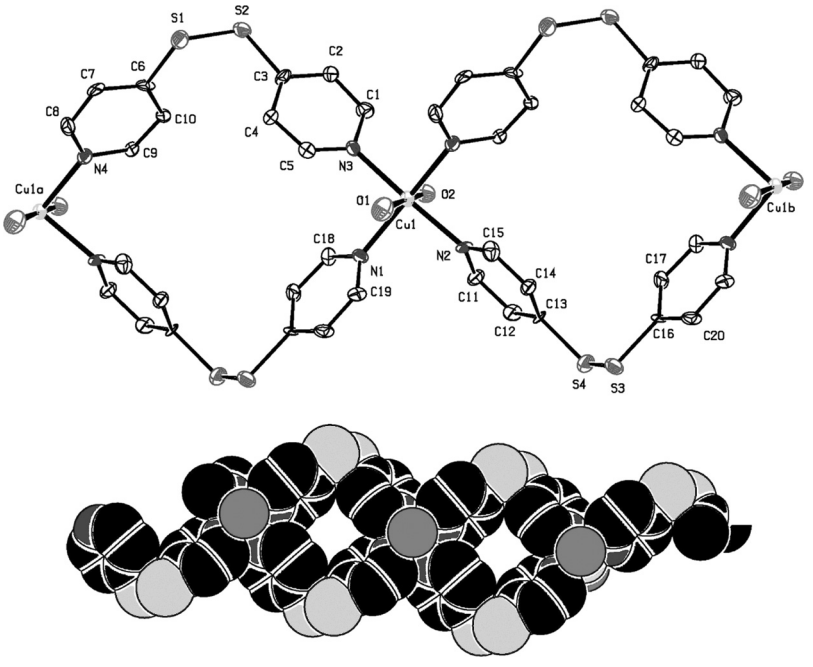

Figure 1. The polymeric structure drawing of the Cu^{II} ion coordination with the atom numbering scheme, and space-filling representation of the double-stranded chain. The H atoms and triflate anion have been omitted for clarity.

bpds ligands [31], and larger than that in the free ligand 83.8(3)° [26] which seems to indicate a strong deformation when the ligand is coordinated to the metal ion. The S–S bond length of 2.020(5) Å is shorter than the value found in the free ligand (2.032(4) Å). The C–S bonds ranging from 1.768–1.801 Å are almost single bonds. The pyridine ring mean planes form a dihedral angle of 73.0(5)°. This bpds conformation spans the copper ions at a distance of 10.357(4) Å, which coincides with the length of the unit cell along the a axis. Each copper center is bridged by two dpds ligands to form a double-stranded chain (Fig. 1). As in other double-stranded chain complexes [32,33] two copper atoms and two dpds ligands form a metallacycle in which the non-bonded distance between the two copper atoms ranging 9.944–11.119 Å (Table 2). The dimensions of the distorted square cavity are ca. 5×5 Å. This molecular box is twisted to make the enclosed cavity a small one, resulting from the flexibility of bpds ligand and the hexacoordinated geometry of the Cu^{II} ion. The resulting chains undergo H-bonding which origin from the fluor atoms of the triflate counter ions and hydrogen atom of coordinated water molecules resulting in a 2D supramolecular network in the solid state, generating a graph-set motif $C_4^4(12)$ ring [34b], Figure 2. The hydrogen-bonding parameters are as follows: O ··· F F distances and O—H ··· F angles are 2.793(9), 3.082(9) Å and 147, 161°, all being in the normal range of such weak interactions [34]. The compound present weak C—H ··· S intramolecular hydrogen bonds with C ··· S distances and C—H ··· S angles in the ranges 3.22–3.26 Å and 111–115° respectively.

In the TG-DTG curve, there are four main successive mass loss stages from 50–900°C (Fig. 4). The first mass loss stage (I), starts at 84°C ends at 218°C and reaches the largest rate at 183°C with mass loss percentage of 9.60% of the initial weight. This stage roughly coincides with the value of 10.7%, calculated for the loss of five water molecules, presumably three molecules absorbed from atmosphere water (HR ~ 80%) and two coordinated water molecules. The fully dehydrated sample is then stable towards further thermal degradation until temperatures in excess of 218°C, with no further weight loss noted over the range 172–218°C. The second stage (II), start at 218°C, finishes at 350°C and reaches the largest rate at 280°C . The loss percentage (35.6%) is near the loss of two triflate anions (calculated 36.5%). The

Table 2. Intermetallic distance (Å) in $1D[ML(dpds)_2L]_n$ polymers with metal ions double bridged by two dpds ligand. (M = Fe(II), Mn(II), Cu(II), Zn(II), Co(II), Ir(III))

Ligand L	M–M (Å)	C–S–S–C (°)	Reference
SCN	10.965	91.17	[37]
N3	11.119	90.32	[38]
SO_4^{-2}	10.547	88.38	[39]
$(CH_3)SO$	10.817	88.75	[39]
H_2O	10.855	90.24	[40]
N_3	10.839	92.19	[41]
MoS_3O	9.772	−79.39	[42]
SCN	10.832	89.96	[43]
$C_2O_4^{-2}, H_2O$	9.944	−87.42	[44]
ClO_4^-	10.702	91.67	[45]

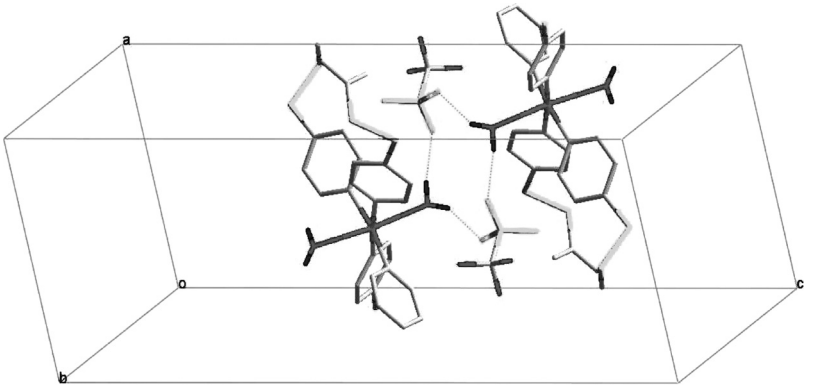

Figure 2. The crystal structure showing the 2D supramolecular network.

third stage (III), start at 350°C ends at 422°C and reaches the largest rate at 380°C. The loss percentage (24.4%) is near the loss of one dpds molecule (calculated 26.2%). The four stage (IV), start 422 ends at 590°C and reaches the largest rate at 500°C. The loss percentage (22.3%) is near the loss of one dpds molecule (calculated 26.2%) then succeeded by the decomposition of the coordination polymer and formation of Cu (found 4.5%, calculated 7.5%). The IR spectrum of final residue indicates that all 4,4′-dipyrydildisulfide ligands have decomposed. In conclusion, on the basis of the TG-DTG, the thermal decomposition processes of $[Cu(dpds)_2(H_2O)_2]\ 2\cdot tft\cdot 4H_2O$ are predicted as follows:

$$[Cu(dpds)_2(H_2O)_2]\ 2\cdot tft\cdot 3H_2O \xrightarrow[-5H_2O]{84\text{-}218^{o}C} [Cu(dpds)_2]2\cdot tft$$

$$[Cu(dpds)_2]2\cdot tft \xrightarrow[-2tft]{218\text{-}350^{o}C} [Cu(dpds)_2]$$

$$[Cu(dpds)_2] \xrightarrow[-dpds]{350\text{-}422^{o}C} [Cu(dpds)]$$

$$[Cu(dpds)] \xrightarrow[-dpds]{422\text{-}590\ ^{o}C} Cu$$

The reflectance spectra in the solid state (Fig. 3) were recorded in the range 200–100 nm. The visible reflectance spectra for the title compound contain only one band at 592 nm, characteristic of a d^9 copper (II) $dx_2\text{-}y_2 \rightarrow dxz\ dyz$ transition via ($2B_{1g} \rightarrow 2E_g$) [35,36] in a square-planar geometry (or elongated octahedron), with

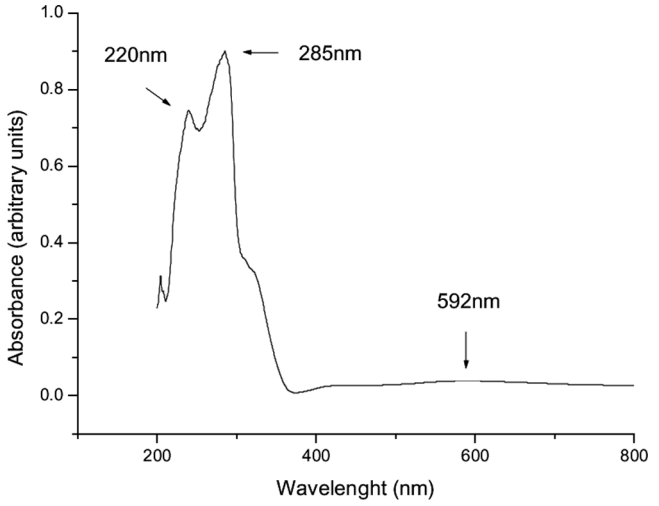

Figure 3. Diffuse reflectance spectrum for the title compound.

the unpaired electrons mainly located in the dx_2-y_2 orbital. When in a complex of octahedral symmetry, the ligands are in trans position with respect to the metal, suffer a tetragonal distortion, the orbital of these ligands interact more weakly on the z axis, those z-components orbitals (dz^2, dxz, dyz) will be stabilized and those without z component will be destabilized (Jahn Teller effect), causing a splitting of the orbital T_{2g} and E_g. This splitting, causes d-d broad bands in the ligand field, product of the increased possibilities of electronic transitions, these possibilities are: (a) $2B_{1g} \rightarrow 2A_{1g}$, (b) $2B_{1g} \rightarrow 2B_{2g}$, (c) $2B_{1g} \rightarrow 2E_g$. According to the selection rules for a system D_{4h}, these transitions are orbitally forbidden, however, the transitions (a) and (c) are vibrationally allowed, through the vibrational coupling, through B_{2u}

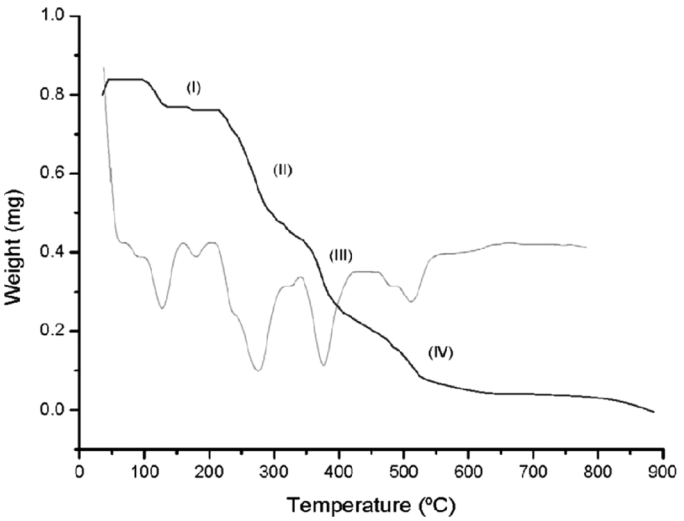

Figure 4. TG-DTG curve for the title compound.

and E_u vibrational modes. These vibrationally allowed bands are weak and is responsible of the low intensity of the d-d band of the title compound. There are two bands with the longer (385 nm) and shorther-wavelength (220 nm) absortions corresponding to the intraligand $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively.

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