



Crystal structure, characterization and magnetic properties of a 1D copper(II) polymer incorporating a Schiff base with carboxylate side arm

Shyamapada Shit, Madhusudan Nandy, Corrado Rizzoli, Cédric Desplanches, Samiran Mitra

► To cite this version:

Shyamapada Shit, Madhusudan Nandy, Corrado Rizzoli, Cédric Desplanches, Samiran Mitra. Crystal structure, characterization and magnetic properties of a 1D copper(II) polymer incorporating a Schiff base with carboxylate side arm. *Journal of Chemical Sciences*, 2016, 128 (6), pp.913-920. 10.1007/s12039-016-1082-4 . hal-01337203

HAL Id: hal-01337203

<https://hal.science/hal-01337203>

Submitted on 2 Feb 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Crystal structure, characterization and magnetic properties of a 1D copper(II) polymer incorporating a Schiff base with carboxylate side arm

SHYAMAPADA SHIT^{a,b}, MADHUSUDAN NANDY^a, CORRADO RIZZOLI^c,
CÉDRIC DESPLANCHES^{d,e} and SAMIRAN MITRA^{a,*}

^aDepartment of Chemistry, Jadavpur University, Kolkata, West Bengal, 700 032, India

^bDepartment of Chemistry, Jalpaiguri Government Engineering College, Jalpaiguri, West Bengal, 735 102, India

^cUniversità degli Studi di Parma, Dipartimento di Chimica, Parco Area delle Scienze 17/A, I-43124 PARMA, Italy

^dCNRS, ICMCB, UPR 9048, F-33600 Pessac, France

^eUniv. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France

e-mail: samiranju92@gmail.com

MS received 18 December 2015; revised 19 March 2016; accepted 22 March 2016

Abstract. A new 1D polymeric copper(II) complex $[\{\text{Cu}(\text{L})(\text{CF}_3\text{COO})\}_2]_n$ has been synthesized using a potentially tetradentate Schiff base ligand, HL, ((E)-2-((pyridin-2-yl)methyleneamino)-5-chlorobenzoic acid) and characterized by different spectroscopic methods. Single crystal X-ray structural characterization reveals that the side arm carboxylate group of the coordinated Schiff base exhibits a $\mu_{1,3}$ -bridging mode and connects the neighbouring copper(II) ions leading to a zigzag 1D chain structure where the copper(II) ions display distorted square pyramidal geometries. Variable temperature magnetic susceptibility measurement reveals a weak antiferromagnetic exchange ($J = -0.47 \pm 0.01 \text{ cm}^{-1}$) prevails between copper(II) ions in the chain mediated by the bridging carboxylate group, is also supported by the room temperature EPR spectral study. Electrochemical property of the complex is also reported.

Keywords. 1D copper(II) polymer; Schiff base; crystal structure; electrochemistry; EPR; magnetic properties.

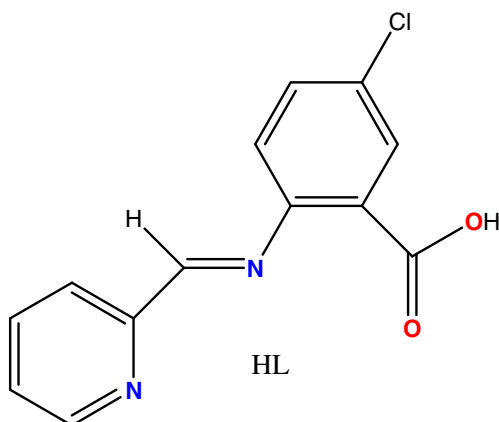
1. Introduction

The design and construction of coordination polymers based on transition and non-transition metal ions are of long standing interest to chemists and material scientists for their rich structural features and potential applications as functional materials.^{1–11} Careful selection of ligands having capacities to combine more than one metal centre or by using different spacer ligands for connecting metals in combination with other co-ligands are considered as important strategies for the synthesis of these complexes in addition to the effect of reaction conditions and solvents.^{2–5} Sometimes, suitable secondary building units (SBU) are also used as important tools for the design and synthesis of these coordination polymers.⁶ Schiff bases owing to their facile syntheses, tunable steric and electronic properties have also been extensively employed over the years for this purpose, leading to coordination polymers of fascinating structures and rich topological features. Role of various Schiff bases/blockers and azide as bridging ligand in a

number of copper(II) poly-clusters/assemblies may be mentioned in this regard not only for the structural diversities of the resulting complexes but also for their potential applications in the field of molecular magnetism.^{7,8} The role of the Schiff base ligands with free carboxylate arm also deserved attention in this regard for their abilities to act simultaneously as chelator and bridge to the metals leading to wide varieties of structures. Amino acid-based Schiff bases, a class of the Schiff bases with carboxylate side arm, and their metal complexes were synthesized and studied extensively for their wide applications in biology, pharmacy and industry.^{12–25} However, little focus has been given to the class of amino acid Schiff bases obtained by condensation of carbonyl compounds and aromatic amines with carboxylic acid side arm in spite of bearing similar free carboxylate end which is considerably flexible from the point of view of the steric orientation in the formation of less strained covalent bonds with the metal centers with potential to show versatile bridging modes.

As a contribution to the work on metal complexes derived from Schiff base ligands incorporating a carboxylate side arm, we have reported a few complexes

*For correspondence



Scheme 1. Schiff base ligand (HL): (E)-2-((pyridin-2-yl)methyleneamino)-5-chlorobenzoic acid.

in recent past.^{26–30} As a continuation of the work on metal complexes based on Schiff bases incorporating a bridging carboxylate, we report herein a new 1D copper(II) complex, $[\{Cu(L)(CF_3COO)\}_2]_n$, derived from a Schiff base ligand HL, ((E)-2-((pyridin-2-yl)methyleneamino)-5-chlorobenzoic acid) (scheme 1), and characterized by micro-analytical, FT-IR, UV-Vis, and EPR spectroscopic methods.

Single crystal X-ray structural characterization reveals that polymeric chain propagates in a *zigzag* manner through $\mu_{1,3}$ -carboxylato bridging in a *syn-anti* fashion incorporating copper(II) ions in distorted square pyramidal geometry. Low temperature susceptibility measurements reveal its weak antiferromagnetic behavior ($J = -0.47 \pm 0.01 \text{ cm}^{-1}$) which is well-supported by the EPR studies. Its redox properties were also investigated.

2. Experimental

2.1 Materials and Methods

2-Amino-5-chlorobenzoic acid and 2-pyridinecarboxaldehyde were purchased from Aldrich Chemical Co. and used without further purification. Hydrated copper(II) trifluoroacetate was prepared by the treatment of basic copper(II) carbonate, $CuCO_3 \cdot Cu(OH)_2$ (AR grade, E. Merck, India) with 60% trifluoroacetic acid (AR grade, E. Merck, India) followed by slow evaporation on steam-bath, filtration through a fine glass frit, and storage in $CaCl_2$ desiccator for subsequent use. All other chemicals and solvents were of analytical reagent grade and used as received. Elemental analyses (carbon, hydrogen and nitrogen) were carried out with a Perkin Elmer 2400 II elemental analyzer. The copper content of the complex was estimated quantitatively

by standard iodometric procedure. The FT-IR spectra ($4000\text{--}400 \text{ cm}^{-1}$) were recorded on a Perkin Elmer Spectrum RX I FT-IR system with solid KBr pellets. The electronic spectra were recorded on a Perkin Elmer Lambda 40 UV-Vis spectrometer using HPLC grade acetonitrile as solvent. Electrochemical measurements were performed using a PAR VersaStat-potentiostat/Galvanostat II electrochemical analysis system under dry argon using conventional three electrode configuration in acetonitrile with tetrabutylammonium perchlorate as the supporting electrolyte. Platinized platinum millielectrode and saturated calomel electrode (SCE) were used as working and reference electrodes, respectively, along with a platinum counter electrode in cyclic voltammetry, performed at various scan rates ($\nu = 30, 50, 70, 100, 150, \text{ and } 200 \text{ mV sec}^{-1}$). Variable temperature magnetic susceptibility measurements were carried out with a Quantum Design MPMS-5S SQUID magnetometer under an applied magnetic field of 5000 Oe on a polycrystalline sample in the temperature range 5–300 K. Diamagnetic corrections were estimated from Pascal's tables and magnetic data were corrected for diamagnetic contributions of the sample holder. X-band EPR spectrum was recorded at room temperature on the solid sample using a Jeol JES-FA 200 ESR spectrometer. Powder X-ray diffraction was performed on a Bruker D8 instrument with $Cu \text{ K}\alpha$ radiation.

2.2 Synthesis of Schiff base and its copper(II) complex

The Schiff base (HL, ((E)-2-((pyridin-2-yl)methyleneamino)-5-chlorobenzoic acid)) was prepared following our published procedure.³⁰ The complex was prepared as follows: 10 mL of the methanolic solution of the Schiff base HL (0.261 g, 1 mmol) was added to another methanolic solution (10 mL) of copper(II) trifluoroacetate (0.290 g, 1 mmol) hydrate with slow stirring over a period of 30 min. The resulting blue colored solution was filtered and the filtrate was kept undisturbed at room temperature for seven days. Light blue crystals suitable for X-ray diffraction were obtained by slow evaporation of the mother liquor. Yield: 82% (based on metal substrate). Anal. Calcd (%) for $C_{30}H_{16}Cl_2Cu_2F_6N_4O_8$: C, 41.30; H, 1.85; N, 6.42; Cu, 14.57; Found (%): C, 41.22; H, 1.81; N, 6.39; Cu, 14.56.

2.3 X-ray crystallography

A plate shaped blue crystal of the complex was mounted on a Bruker APEX2 CCD diffractometer equipped with graphite monochromatized fine focus sealed tube molybdenum target ($MoK\alpha = 0.71073 \text{ \AA}$). Data

collections were performed at 294(2) K using ω scan technique. Data collection was performed with the APEX2³¹ software while cell refinement and data reduction were performed with the SAINT program.³¹ Multi-scan absorption corrections were applied to the intensity values ($T_{\max} = 0.908$ and $T_{\min} = 0.780$) using SADABS.³¹ The structure was solved by direct methods with SIR97³² and refined by full-matrix least square method based on F^2 with SHELXL-97³³ programs. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed geometrically and refined with isotropic thermal parameters using a riding model approximation. The carbon and fluorine atoms (C30, F4, F5, and F6) of one trifluoromethyl group were rotationally disordered over two orientations with occupancy ratio of 0.70: 0.30. During the refinement, the C–F bond lengths and F...F separations within the disordered group were constrained to be 1.32(1) and 2.16(2) Å, respectively. The disordered atoms were also restrained to have similar U_{ij} components using the SIMU command in SHELXL-97.³³

Table 1. Crystal and structure refinement data for $\{[\text{Cu}(\text{L})(\text{CF}_3\text{COO})]_2\}_n$.

Formula	$\text{C}_{30}\text{H}_{16}\text{Cl}_2\text{Cu}_2\text{F}_6\text{N}_4\text{O}_8$
Formula weight	872.45
Crystal dimension (mm)	$0.06 \times 0.11 \times 0.16$
Crystal system	Orthorhombic
Space group	$P2_12_12_1$ (No. 19)
a (Å)	8.8555(16)
b (Å)	16.944(3)
c (Å)	21.303(3)
V (Å ³)	3196.5(9)
Z	4
T (K)	294(2)
$\lambda_{\text{Mo-K}\alpha}$ (Å)	0.71073
D_c (g cm ⁻³)	1.813
μ (mm ⁻¹)	1.592
$F(000)$	1736
θ range (°)	1.9–25.5
Index ranges	$-10 \leq h \leq 10$, $-20 \leq k \leq 20$, $-25 \leq l \leq 25$
Total data	35503
Unique data	5796
Observed data [$I > 2\sigma(I)$]	4701
N_{ref} ; N_{par}	5796; 506
Final R Indices [$I > 2\sigma(I)$]	$R1 = 0.0455$ $wR2 = 0.1037$
R indices (all data)	$R1 = 0.0581$ $wR2 = 0.1113$
R_{int}	0.057
Goodness-of-fit on F^2	1.039
$\Delta\rho_{\text{min}}$ (e.Å ⁻³)	−0.39
$\Delta\rho_{\text{max}}$ (e.Å ⁻³)	2.32

The structure was refined as an inversion twin, the refined ratio of the twin components obtained by the TWIN/BASF procedure³³ being 0.614(17):0.386(17). All calculations and graphical illustrations for the complex have been done using WinGX,³⁴ ORTEP,³⁵ and SCHAKAL³⁶ programs. Selected crystallographic data and some important structure refinement parameters of the complex are summarized in table 1.

3. Results and Discussion

3.1 Crystal structure of the complex

An ORTEP view of the asymmetric unit of the complex with atom numbering scheme is shown in figure 1 and relevant bond lengths and angles are summarized in table 2. The asymmetric unit consists of two chemically similar but crystallographically independent copper(II) centers.

Each copper(II) center is penta-coordinated in a distorted square-pyramidal geometry by similar donor sets, where the Schiff base ligands act as tridentate with respect to one copper centre, whereas they are in fact tetradentate when the bridging mode of the carboxylato groups is considered. The basal plane about Cu1 is provided by the pyridine nitrogen (N2), the imine nitrogen (N1), and one carboxylato oxygen atoms (O1) of the same Schiff base and one oxygen atom (O3) of a monodentate trifluoroacetate ion, and the apical position is occupied by one carboxylato oxygen of a symmetry related ligand (O6ⁱ, $i = -1+x, y, z$). Similarly, the basal plane of the square pyramidal geometry about Cu2 is

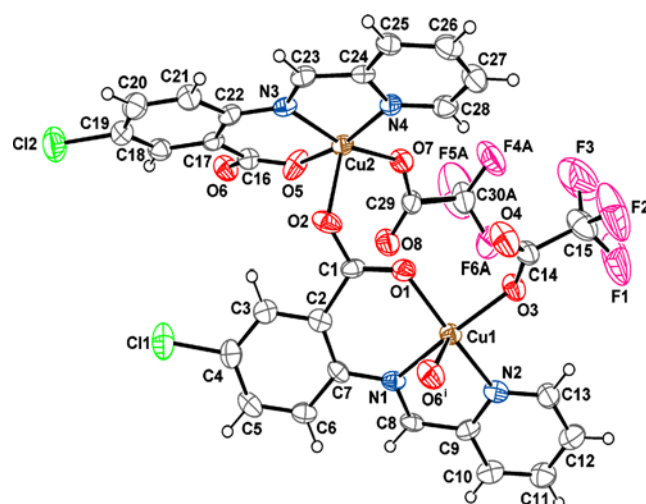


Figure 1. An ORTEP view of the asymmetric unit of the complex with displacement ellipsoids drawn at the 40% probability level. Only the major component of disorder affecting one trifluoromethyl group is shown. Symmetry code: (i) $-1+x, y, z$.

occupied by the N4, N3, O5 and O7 atoms and the apical position by the O2 atom of the Schiff base ligand coordinated to the Cu1 centre. The O2 and O1 carboxylato oxygen atoms of the Schiff base ligands are coordinated to two adjacent copper(II) ions in a $\mu_{1,3}$ -, *syn-anti* fashion. The donor atoms occupying the basal sites are coplanar within ± 0.05 Å for Cu1 and ± 0.008 Å for Cu2, indicating electron delocalization over the ligand. The metals are displaced from the least squares mean basal plane by 0.2634(5) and 0.2159(5) Å toward the apical oxygen atom for Cu1 and Cu2, respectively. The distortion of the coordination polyhedra is also evident from the values of the bond angles (table 2).

The τ value,³⁷ an index of degree of trigonality, is 0.07 and 0.03 for Cu1 and Cu2, respectively, which

indicates the distortion from the ideal square-pyramidal geometry. The bond lengths involving the two independent copper ions (mean values: Cu–N(pyridine) = 2.0075(9) Å; Cu–N(azomethine) = 2.014(3) Å; Cu–O(carboxylato, basal) = 1.899(5) Å; Cu–O(carboxylato, apical) = 2.170(9) Å; Cu–O(trifluoroacetato) = 1.9399(9) Å) are not significantly different.

The crystal packing also shows that the bridging Cu–O–C–O–Cu pathway leads to a helical chain polymer running parallel to the crystallographic *a* axis as shown in figure 2. The polymeric chains are linked into a 2D sheet structure through weak inter-chain C–H...O hydrogen bond interactions (table 3).

The complex reported herein may be compared to our earlier reported one,²⁶ as both were derived from Schiff base ligands having the same donor sets with slight variation of the ligand backbone. Both are helical 1D polymeric in nature but the complex reported herein consists of dimeric asymmetric unit with two crystallographically independent copper(II) ions compared to the unique type of copper(II) atom in the earlier one. The presence of an electron withdrawing chlorine substituent in the ligand backbone of the complex may be responsible for strengthening the association of the two copper(II) ions in the asymmetric unit.³⁸ This is also evident from the slightly shorter Cu...Cu separation (5.2650(10) Å) in the polymeric chain compared to the separations of 5.2827(19) Å in the complex reported earlier.²⁶

3.2 Infrared spectra

In the FT-IR spectrum of HL (figure S1 in Supplementary Information), an intense absorption band

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

Bond lengths			
Cu1–O1	1.904(3)	Cu2–O2	2.162(4)
Cu1–O3	1.941(3)	Cu2–O5	1.895(3)
Cu1–N1	2.011(3)	Cu2–O7	1.939(3)
Cu1–N2	2.006(4)	Cu2–N3	2.017(3)
Cu1–O6 ⁱ	2.178(3)	Cu2–N4	2.008(4)
Bond angles			
O1–Cu1–O3	92.43(15)	O2–Cu2–O5	93.10(15)
O1–Cu1–N1	92.44(15)	O2–Cu2–O7	106.64(14)
O1–Cu1–N2	161.37(16)	O2–Cu2–N3	86.68(13)
O1–Cu1–O6 ⁱ	93.21(15)	O2–Cu2–N4	98.27(14)
O3–Cu1–N1	165.20(14)	O5–Cu2–O7	92.94(14)
O3–Cu1–N2	89.31(14)	O5–Cu2–N3	92.57(14)
O3–Cu1–O6 ⁱ	105.10(14)	O5–Cu2–N4	167.09(16)
N1–Cu1–N2	81.69(15)	O7–Cu2–N3	165.27(14)
O6 ⁱ –Cu1–N1	88.56(13)	O7–Cu2–N4	89.65(14)
O6 ⁱ –Cu1–N2	104.24(14)	N3–Cu2–N4	82.06(14)

Symmetry code: ⁱ –1+x, y, z

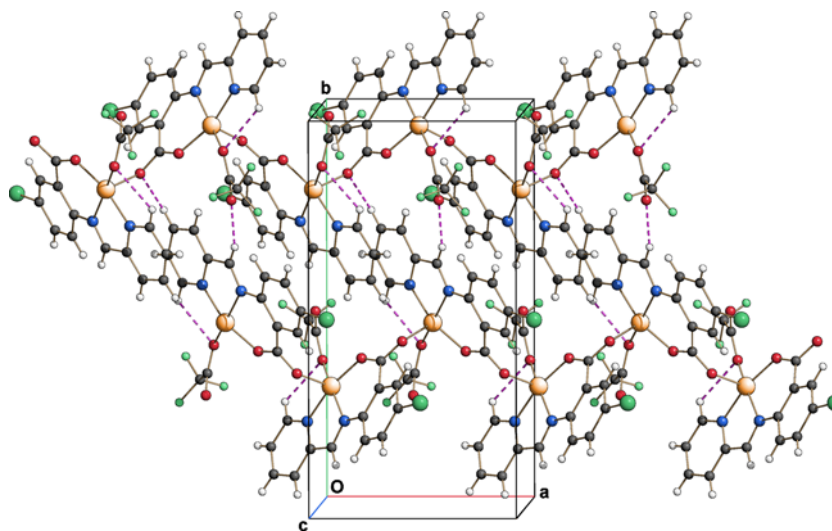


Figure 2. The crystal packing of the complex showing the polymeric chains parallel to the *a*-axis. Hydrogen bonds are shown as dashed lines. Only the major components of the disordered trifluoromethyl groups are shown.

Table 3. Hydrogen bonding parameters (Å, °).

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠ (D-H...A)
C8-H8...O4 ^a	0.93	2.24	3.121(5)	158
C11-H11...O2 ^a	0.93	2.53	3.144(6)	124
C13-H13...O3	0.93	2.50	2.973(6)	112
C23-H23...O8 ^b	0.93	2.23	3.109(5)	158
C26-H26...O6 ^b	0.93	2.59	3.261(6)	129
C28-H28...O7	0.93	2.54	2.998(6)	111

Symmetry codes: (^a) 1-x, 1/2+y, 1/2-z (^b) 2-x, -1/2+y, 1/2-z

corresponding to $\nu_{\text{C=N}}$ (imine group) was observed at 1642 cm^{-1} . Strong bands corresponding to $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ vibrations of the free ligand were observed at 1695 and 1414 cm^{-1} , respectively. A broad band corresponding to $\nu(\text{O-H})$ stretching vibration centered around 3338 cm^{-1} was also observed in the spectrum of the free ligand. Strong sharp bands attributed to the pyridine skeleton of the Schiff base ligand, were observed at 1586 , 1491 and 1430 cm^{-1} .³⁹

In the spectrum of the complex (figure S2 in SI), asymmetric ($\nu_{\text{as}}(\text{COO})$) and symmetric ($\nu_{\text{s}}(\text{COO})$) stretching vibrations of the carboxylate group were observed at 1702 and 1406 cm^{-1} , respectively. The difference ($\Delta\nu$) between $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ is 294 cm^{-1} for the complex indicating the bridging coordination mode of the carboxylate group of the Schiff base.²⁸ The band corresponding to azomethine ($\nu_{\text{C=N}}$) stretching vibration is obscured in the spectrum of the complex probably due to the very strong intensity of the asymmetric stretching vibrations ($\nu_{\text{as}}(\text{COO})$) of the carboxylate group. Bands corresponding to the pyridine skeleton of the Schiff base moiety were observed at 1587 , 1484 , and 1446 cm^{-1} . Coordination of pyridine/azomethine nitrogen to copper(II) were substantiated by very weak bands at 446 and 420 cm^{-1} .

3.3 Electronic spectra

The spectrum of HL (figure S3 in SI) shows a relatively weak band at 335 nm , assigned to the $n \rightarrow \pi^*$ transition of the azomethine group. In addition, two strong bands also appear at 211 and 258 nm , assignable to $\pi \rightarrow \pi^*$ and intra-ligand charge transfer transitions.⁴⁰

In the spectrum of the complex (figure S4 in SI), a broad and low intensity absorption band centered around 708 nm is assigned to the $d-d$ transition for the copper(II) ion in a distorted square pyramidal geometry.⁴¹ Ligand coordination is supported by the appearance of a strong band at 345 nm , corresponding to the ligand to metal charge transfer (LMCT) transition.⁴² $\pi \rightarrow \pi^*$ and intra-ligand charge transfer transition bands of the free ligand are shifted to the

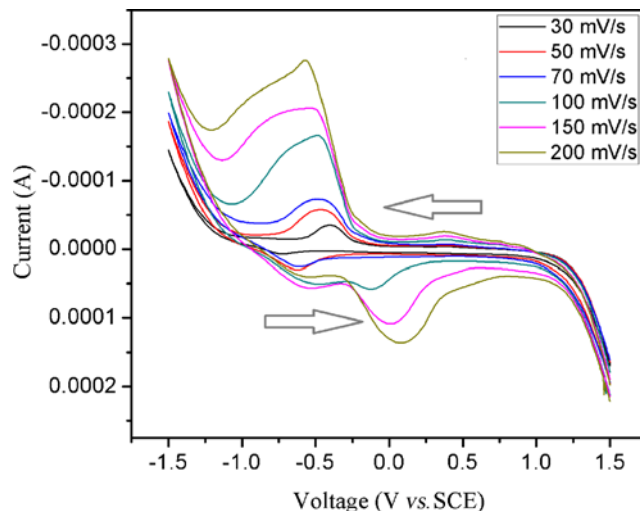


Figure 3. Cyclic voltammograms of the complex recorded in acetonitrile at room temperature.

higher energy region in the spectrum of the complex and appear at 205 and 250 nm , respectively.

3.4 Electrochemical studies

Cyclic voltammogram of the complex (figure 3) was recorded at room temperature in acetonitrile within the potential range of -1.5 to $+1.5\text{ V}$ using tetrabutyl ammonium perchlorate as supporting electrolyte measured at different scan rate of 30 , 50 , 70 , 100 , 150 , 200 mV sec^{-1} . On cathodic scan, only one reductive response corresponding to the $\text{Cu(II)} \rightarrow \text{Cu(I)}$ process was observed at -0.41 , -0.47 , -0.48 , -0.51 , -0.56 , and -0.58 V (versus SCE) for the respective scan rates. Similarly, anodic scan shows only one oxidative response due to the $\text{Cu(I)} \rightarrow \text{Cu(II)}$ process observed at -0.75 , -0.61 , -0.60 , -0.45 , -0.46 , and -0.43 V (versus SCE) for the respective scan rates. Thus, peak-to-peak separations of 340 , 180 , 120 , 60 , 100 , and 150 mV , respectively, suggest the irreversible nature of the redox process. Upon increasing the scan rate, the cathodic peak positions shifted to more negative values and the anodic peak position to more positive values while peak current increased in both scans and

$I_{pc}/I_{pa} > 1$ confirmed the irreversible nature of the redox process. The presence of only one redox couple also confirm that copper(II) centers present in the complex are chemically similar. However, at a higher scan rate (100, 150, and 200 mV sec^{-1}), an additional peak was observed at -0.11 , $+0.01$, and $+0.08$ V, respectively, which tentatively can be assigned to the oxidation of the coordinated Schiff base.^{43,44}

3.5 EPR spectrum

The X-band EPR spectrum of the complex recorded in powder state at room temperature using a 9.5 GHz

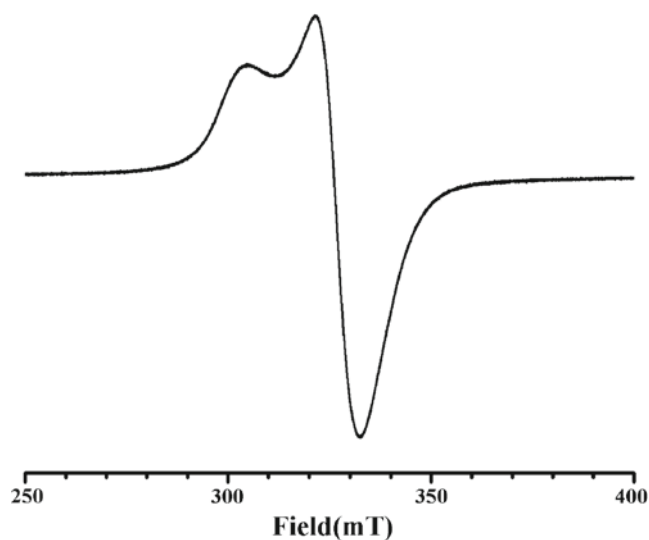


Figure 4. X-band EPR spectrum of the complex recorded at room temperature.

field modulation, shows the presence of an elongated axial symmetry signal without any resolved hyperfine structure (figure 4). The values of the anisotropic parameters of the spectrum are $g_{\parallel} = 2.215$, $g_{\perp} = 2.071$, which are typical values for copper(II) ions with $d_{x^2-y^2}$ ground state. The “half-field” signal is absent which suggests that the magnetic exchange interaction between copper(II) ions through carboxylato bridge is very weak, also confirmed by cryomagnetic susceptibility measurements.^{45,46}

3.6 Magnetic properties

The temperature dependence of the molar magnetic susceptibility, χ_M , was measured on a polycrystalline sample in the temperature range 5–300 K. In figure 5 the experimental points are shown as black squares and the calculated curves in red. Data analysis was done on the $\chi_M T$ versus T plot. The $\chi_M T$ value at room temperature is about $0.425 \text{ cm}^3 \text{ K mol}^{-1}$, in good agreement with one uncoupled spin $S = 1/2$ with a Landé factor $g = 2.14$. The $\chi_M T$ value remains constant down to about 15 K. A very small decrease in $\chi_M T$ was observed when the temperature was further decreased below 15 K, to reach the value of $0.40 \text{ cm}^3 \text{ K mol}^{-1}$ at 5 K (figure 5), indicating weak antiferromagnetic nature of the complex.

Due to the chain structure of the complex, we have used the model of equally spaced copper(II) ions. The spin Hamiltonian in zero-field is $H = -J \sum_{i=1}^{n-1} S_{A_i} \cdot S_{A_{i+1}}$ where the summation runs over the n sites of the chain. When n tends to infinity, there is no analytical method

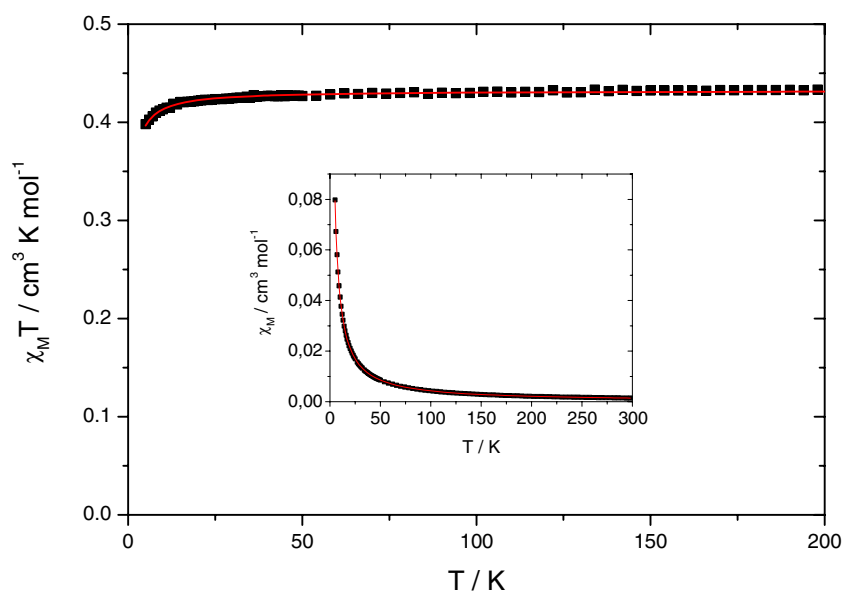


Figure 5. Plot of $\chi_M T$ versus T for the complex. Insert: Plot of χ_M versus T for the complex. The red solid line is the best fit to the data set.

to determine the magnetic susceptibility. However, the results can be fitted using the numerical expression for $J < 0$.⁴⁷

$$\chi_M T = \frac{Ng^2\beta^2}{k} \times \frac{0.25 + 0.0774975x + 0.075235x^2}{1.0 + 0.9931x + 0.172135x^2 + 0.757825x^3}$$

with $x = -J/kT$.

The best fit was obtained for Landé factor $g = 2.14$ and isotropic interaction parameter $J = -0.47 \pm 0.01 \text{ cm}^{-1}$.

Two copper(II) ions are linked by a carboxylate function of the organic ligand. The COO^- bridging function is linked by an oxygen atom to a square pyramid copper(II) atom in basal position, whereas the second oxygen of the COO^- group is linked to a second square pyramid copper(II) ion in the apical position. The weak coupling may be explained as follows: the magnetic orbital describing the unpaired electron on a copper(II) ion in square pyramid is of the $d_{x^2-y^2}$ type (the x and y axes being defined by the short equatorial bonds). These orbitals have thus no component along the apical direction of the square planar copper(II) ion. As the magnetic interaction between two copper(II) ions takes place through this apical direction, the overlap between the magnetic orbitals of two neighbouring copper(II) ions is thus very small. As a consequence, the isotropic interaction parameter J , roughly proportional to the square of the overlap between the magnetic orbitals, is expected to be very small.

3.7 Powder XRD data

The experimental powder XRD pattern of the bulk product of the complex is in good agreement with the simulated XRD pattern obtained from single crystal X-ray diffraction, confirming phase purity of the bulk sample (figure S5 in SI). The simulated pattern was calculated from the single crystal structural data (cif file) using the CCDC Mercury software.

4. Conclusions

Herein we have reported the synthesis, spectral and structural characterization of a new 1D copper(II) coordination polymer derived from a potentially tetradentate Schiff base with a bridging carboxylate side arm. The structural characterization reveals that the differences in the distorted square pyramidal geometry of the two independent copper(II) ions within the asymmetric unit, which are embedded with same donor sets, are negligible. It also reveals that in the polymeric chain neighbouring

copper(II) ions are connected to each other via $\mu_{1,3}$ -carboxylato bridging in a *syn-anti* fashion. Electrochemical studies in acetonitrile indicated only one irreversible redox couple. EPR and low temperature magnetic susceptibility measurements reveal weak antiferromagnetic behaviour of the complex ($J = -0.47 \pm 0.01 \text{ cm}^{-1}$).

Supplementary Information (SI)

All additional information pertaining to characterization of the ligand and complex using IR spectra (figures S1, S2), electronic spectra (figures S3, S4), and simulated and experimental PXRD patterns of the complex (figure S5) are given in the supporting information available at www.ias.ac.in/chemsci.

Acknowledgements

S. Shit gratefully acknowledges University Grants Commission, New Delhi, India for financial assistance (Minor Research Project No. F. PSW-65/12-13 (ERO)). Thanks are also extended to the University Grants Commission, New Delhi, India for financial assistance (Project No. F.6-6/2013-14/EMERITUS-2013-14-GEN-2214/(SA-II)) to Prof. S. Mitra as Emeritus Fellow.

References

1. Eddaoudi M, Kim J, Rosi N, Vodak D, Wachter J, O'Keeffe M and Yaghi O M 2002 *Science* **295** 469
2. Kitagawa S, Kitaura R and Noro S 2004 *Angew. Chem. Int. Ed.* **43** 2334
3. Tripathi S, Srirambalaji R, Singh N and Anantharaman G 2014 *J. Chem. Sci.* **126** 1423
4. Vishnoi P, Kalita A C and Murugavel R 2014 *J. Chem. Sci.* **126** 1385
5. Mudsainiyan R K, Jassal A K, Arora M and Chawla S K 2015 *J. Chem. Sci.* **127** 849
6. Suresh P and Prabusankar G 2014 *J. Chem. Sci.* **126** 1409
7. Mukherjee S and Mukherjee P S 2013 *Acc. Chem. Res.* **46** 2556
8. Mukherjee S, Gole B, Song Y and Mukherjee P S 2011 *Inorg. Chem.* **50** 3621
9. Dybtsev D N, Chun H and Kim K 2004 *Angew. Chem. Int. Ed.* **43** 5033
10. Chen B L, Wang L B, Zapata F, Qian G D and Lobkovsky E B 2008 *J. Am. Chem. Soc.* **130** 6718
11. Horcajada P, Serre C, Maurin G, Ramsahya N A, Balas F, Vallet-Regi M, Sebban M, Taulelle F and Ferey G 2008 *J. Am. Chem. Soc.* **130** 6774

12. Rajesh C M and Ray M 2014 *Dalton Trans.* **43** 12952
13. Kumar N, Khullar S, Singh Y and Manda S K 2014 *Cryst. Eng. Comm.* **16** 6730
14. Thio Y, Toh S W, Xue F and Vittal J J 2014 *Dalton Trans.* **43** 5998
15. Royles B J L and Sherrington D C 2000 *J. Mater. Chem.* **10** 2035
16. Jiang W, Xu B, Liu F, Wang Y and Xiang Z 2015 *Synth. React. Inorg. Metal-Org. Nano-Metal Chem.* **45** 34 (and references therein)
17. Ahmed A H, El-Bahy Z M and Salama T M 2010 *J. Mol. Struct.* **969** 9
18. Puterová-Tokárová Z, Mrázová V, Kožíšek J, Valentová J, Vranovičová B and Boča R 2014 *Polyhedron* **70** 52
19. Malinkin S O, Moroz Y S, Penkova L V, Bon V V, Gumienna-Kontecka E, Pavlenko V A, Pekhnyo V I, Meyer F and Fritsky I O 2012 *Polyhedron* **37** 77
20. Rardin R L, Tolman W B and Lippard S J 1991 *New J. Chem.* **15** 417
21. Sinha D, Tiwari A K, Singh S, Shukla G, Mishra P, Chandra H and Mishra A K 2008 *Eur. J. Med. Chem.* **43** 160
22. Neelakantan M A, Rusalraj F, Dharmaraja J, Johnsonraja S, Jeyakumar T and Pillai M S 2008 *Spectrochim. Acta* **A71** 599
23. Garnovskii A D, Vasilchenko I S, Garnovskii D A and Kharisov B I 2009 *J. Coord. Chem.* **62** 151
24. Vigato P A and Tamburini S 2004 *Coord. Chem. Rev.* **248** 1717
25. Pramanik H A R, Das D, Paul P C, Mondal P and Bhattacharjee C R 2014 *J. Mol. Struct.* **1059** 309
26. Dey S K, Bag B, Malik K M A, El Fallah M S, Ribas J and Mitra S 2003 *Inorg. Chem.* **42** 4029
27. Choudhury C R, Datta A, Gramlich V, Hossain G M G, Malik K M A and Mitra S 2003 *Inorg. Chem. Commun.* **6** 790
28. Sen S, Mitra S, Luneau D, El Fallah M S and Ribas J 2006 *Polyhedron* **25** 2737
29. Shit S, Chakraborty J, Samanta B, Pilet G and Mitra S 2009 *J. Mol. Struct.* **919** 361
30. Shit S, Sasmal A, Dhal P, Rizzoli C and Mitra S 2016 *J. Mol. Struct.* **1108** 475
31. Bruker 2008 *APEX2* (Version 2008.1-0), *SAINT* (Version 7.51A) and *SADABS* (Version 2007/4) (Bruker AXS Inc.: Madison, Wisconsin, USA)
32. Altomare A, Burla M C, Camalli M, Casciaro G, Giacovazzo C, Guagliardi A, Moliterni A G G, Polidori G and Spagna R 1999 *J. Appl. Cryst.* **32** 115
33. Sheldrick G M 2008 *Acta Cryst.* **A64** 112
34. Farrugia L J 1999 *J. Appl. Cryst.* **32** 837
35. Farrugia L J 1997 *J. Appl. Cryst.* **30** 565
36. Keller E 1999 *SCHAKAL-99: Program for Representation of Crystallographic Models* (University of Freiburg: Freiburg, Germany)
37. Addison A W, Rao T N, Reedijk J, van Rijn J and Verschoor G C 1984 *J. Chem. Soc. Dalton Trans.* 1349
38. Shit S, Yadava U, Saha D and Fröhlich R 2013 *J. Coord. Chem.* **66** 66
39. Nakamoto K 1997 In *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (Part A and B) 5th ed. (New York: John Wiley)
40. Lever A B P 1984 In *Inorganic Electronic Spectroscopy* 2nd ed. (Amsterdam: Elsevier)
41. Shit S, Talukder P, Chakraborty J, Pilet G, El Fallah M S, Ribas J and Mitra S 2007 *Polyhedron* **26** 1357
42. Tandon S S, Chander S and Thompson L K 2000 *Inorg. Chim. Acta* **300–302** 683
43. Vijayaraj A, Prabu R, Suresh R, Sivaraj C, Raaman N and Arayanan V 2011 *J. Coord. Chem.* **64** 637
44. Al-Hazmi G A, El-Shahawi M S, Gabr I M and El-Elasmy A A 2005 *J. Coord. Chem.* **58** 713
45. Hathaway B J 1972 *J. Chem. Soc. Dalton Trans.* 1196
46. Tian L, Chen Z, Yu A, Song H-B and Cheng P 2012 *CrystEngComm* **14** 2032
47. Estes W E, Gavel D P, Hatfield W E and Hodgson D 1978 *Inorg. Chem.* **17** 1415