

A new Cu(II) bridging-carboxylate helical chain polymer: synthesis and structural aspects

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The crystal structure of a new Cu(II) carboxylato-bridged complex $[\text{Cu}(\text{L})(\text{SCN})]_n$ (**1**) [where HL = 2-*N*-(2'-pyridylimine)benzoic acid] forms a helical chain polymer chain. In **1**, adjacent copper atoms are linked by carboxylate groups in a *syn-anti* conformation. The title complex was also characterised by elemental analysis, IR spectra, electronic spectra and variable temperature magnetic measurements.

Keywords: tridentate Schiff base, carboxylato-bridged, helical chain polymer, crystal structure, magnetic studies

The structural and chemical factors governing electronic exchange coupling, mediated by bridging ligands, are of continuing interest for bioinorganic chemists. Inorganic chemists are seeking to design new molecular materials with useful optical and electrical properties, by systematic study of their molecular structure.¹⁻³ This information is also applicable to the investigation of metalloprotein active sites with interacting paramagnetic centres. In this regard, studies on metal carboxylate complexes as models for metalloproteins have been investigated extensively.⁴⁻⁶ Moreover, since carboxylate ligands in metalloproteins are provided by amino acid side chains, polydentate chelating ligands containing carboxylate groups are of biological relevance.⁷

Carboxylate as a bridging ligand has been extensively studied, with its widespread applications in bioinorganic chemistry.^{4,8} It gives rise to a wide variety of polynuclear complexes ranging from discrete entities to three-dimensional systems.⁹⁻¹¹ In these complexes, a carboxylate group can assume many types of bridging (*syn-syn*, *anti-anti*, *syn-anti*) and chelating conformations.¹² Generally, the *syn-syn* conformations are seen in dinuclear complexes while the *anti-anti* or *syn-anti* modes are visible in chain or layer compounds.¹³ Colacio and coworkers have shown that tridentate ligands with carboxylate groups can undergo self-assembly processes promoted by metal ions leading to either *anti-anti* or *syn-anti* carboxylate-bridge copper(II) complexes.¹³ Thus, from $[\text{M}(\text{hfac})_2]$ ($\text{M} = \text{Mn}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II})$; hfac = hexafluoroacetylacetonate) and the tridentate ligand derived from 2-imidazole-carboxaldehyde and β -alanine (H_2L^1), *anti-anti* zigzag-chain $[\text{M}(\text{HL}^1)(\text{hfac})]_n$ complexes were obtained,¹² whereas from [(carboxyphenyl)azo]pyrimidine tridentate ligands and copper(II) perchlorate, a series of oligomeric copper(II) complexes could be prepared.¹³ Some examples of structurally and magnetically characterised singly *syn-anti* carboxylate-bridged copper(II) complexes reported so far are described elsewhere.¹³⁻¹⁸

Within this framework and with the aim of preparing new carboxylato-bridged copper(II) complexes, we report here the synthesis and structural characterisation of a new Cu(II) carboxylato-bridged complex with an infinite helical chain polymer (**1**) using the tridentate Schiff base [2-*N*-(2'-pyridylimine) benzoic acid, a product of refluxing [pyridine-2-carboxaldehyde (2 mmol) and anthranillic acid (2 mmol) in methanol]. The crystal structure study also shows that the

Cu(II) atom achieves a distorted square pyramidal geometry as part of the polymeric chain.

The molecular structure of **1**, along with the atom numbering scheme, is shown in Fig. 1 and the selected bond distances and bond angles are listed in Table 2. The structure features a monodeprotonated ligand which is acting as a tridentate ligand towards a Cu(II) atom, whilst simultaneously acting as a monodentate ligand towards a neighbouring Cu(II) centre. The tridentate carboxylate ligands do not saturate the coordination positions on the Cu(II) centre, so self-assembly reactions may occur through the deprotonated carboxylate groups, yielding *syn-anti* carboxylate-bridged polynuclear complexes.¹⁹

In the polymeric chain (Fig. 2) the Cu(II) ions have distorted square-based pyramidal coordination geometry, according to the procedure described by Addison.²⁰ At each copper centre (Fig. 1), the basal positions are occupied by the N(1), N(17) and O(1) atoms of the tridentate Schiff base and the N(2) atom of the terminal thiocyanate. The deviation of the copper atom from this basal plane is 0.270(2) Å towards O(2A) which occupies the axial site. This is the link in the chain and is part of the another tridentate Schiff base ligand. The axial bond distance is longer [Cu(1)–O(2A), 2.191(9) Å] than the equatorial bond distances [Cu(1)–N(2), Cu(1)–N(1), Cu(1)–N(17) and Cu(1)–O(1), 1.975(12), 2.000(9), 2.020(9) and 1.939(7) Å respectively]. The largest deviations from square pyramidal are in the bond angles involving the *trans*

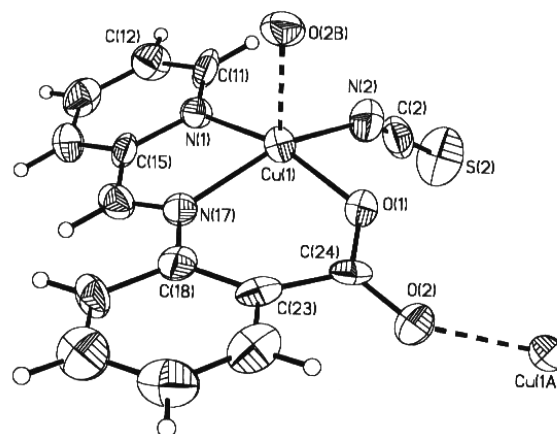
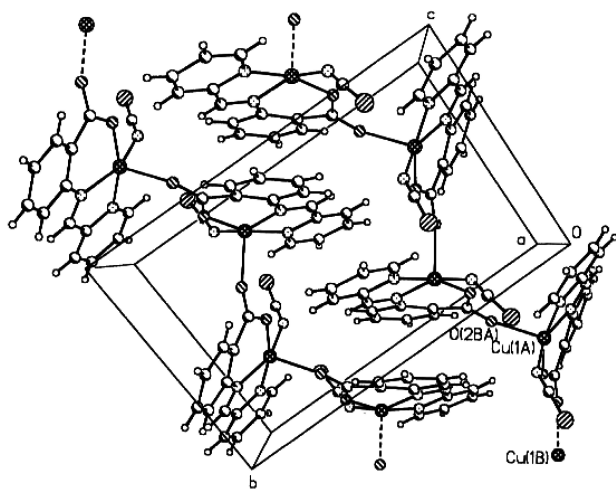


Fig. 1 Molecular structure and crystallographic numbering scheme for **1**.

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Table 1 Crystallographic data for **1**

Empirical formula	C ₁₄ H ₉ CuN ₃ O ₂ S
Formula weight	346.84
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 11.020(2) <i>b</i> = 13.816(2) <i>c</i> = 9.819(2) Å β = 116.170(10)°
Volume	1341.7(4) Å ³
<i>Z</i>	4
Density (calculated)	1.717 g/cm ³
Crystal size	0.34 × 0.28 × 0.08 mm ³
Reflections collected	2759
Independent reflections	2322 [<i>R</i> (int) = 0.1331]
Data / parameters	2322 / 190
Goodness-of-fit on <i>F</i> ²	0.942
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0806, <i>wR</i> 2 = 0.1462
<i>R</i> indices (all data)	<i>R</i> 1 = 0.2306, <i>wR</i> 2 = 0.2044
Largest diff. peak and hole	0.661 and -0.704 e.Å ⁻³

**Fig. 2** Formation of the polymer chain in the crystal structure of **1**.

pairs [157.1(5) and 164.7(4)° for N(2)–Cu(1)–N(17) and N(1)–Cu(1)–O(1) respectively].

There are two chelate rings, one five membered and one six membered. The former, involving the N-bound parts of the Schiff base, is planar as a consequence of the delocalisation of the ligand in that portion. The six membered ring involving the carboxylate part of the chelating ligand has a half chair conformation.

The carboxylate bridge is twisted out of the plane of the aromatic ring 21(2)° for O(2) to be coordinated in an apical position to the next copper in the chain forming an infinite helical chain parallel to the *c* axis. The carboxylate group bridges two Cu(II) ions with the intrachain Cu...Cu distance of 5.370 Å which is long in comparison with other recently reported copper carboxylate complexes (Cu...Cu 4.616, 4.840, 5.186, 5.158 Å).¹⁹

Thermogravimetric analysis shows that the complex **1** is stable up to 105 °C. The mass loss in the TGA curve corresponds to the release of one coordinated thiocyanate group per [Cu(μ-L)(SCN)] unit in the temperature range 105–205 °C. The second step involves the release of one molecule of the Schiff base ligand [HL = C₁₃H₉N₂O₂] in the 205–565 °C temperature range.

The IR spectrum for complex **1** shows bands at 1703 and 1395 cm⁻¹ assigned as ν_{as}(COO⁻) and ν_{sym}(COO⁻) respectively and the difference (Δν) is 308 cm⁻¹ suggests the bridging mode of the carboxylate group.²¹ The ν(C≡N) stretching frequency

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

Cu(1)–O(1)	1.939(7)
Cu(1)–N(2)	1.975(12)
Cu(1)–N(1)	2.000(9)
Cu(1)–N(17)	2.020(9)
Cu(1)–O(2A)	2.191(9)
O(1)–C(24)	1.273(11)
O(2)–C(24)	1.239(12)
N(1)–C(11)	1.314(13)
N(1)–C(15)	1.362(14)
N(2)–C(2)	1.146(16)
S(2)–C(2)	1.614(17)
C(16)–N(17)	1.279(13)
N(17)–C(18)	1.422(13)
O(1)–Cu(1)–N(2)	90.3(4)
O(1)–Cu(1)–N(1)	164.7(4)
N(2)–Cu(1)–N(1)	91.2(4)
O(1)–Cu(1)–N(17)	90.8(4)
N(2)–Cu(1)–N(17)	157.1(5)
N(1)–Cu(1)–N(17)	81.9(4)
O(1)–Cu(1)–O(2A)	93.0(3)
N(2)–Cu(1)–O(2A)	101.7(4)
N(1)–Cu(1)–O(2A)	101.5(3)
N(17)–Cu(1)–O(2A)	101.0(3)
N(2)–Cu(1)–O(1)–C(24)	-156.1(10)
N(1)–Cu(1)–O(1)–C(24)	-60.2(19)
N(17)–Cu(1)–O(1)–C(24)	1.0(10)
O(2A)–Cu(1)–O(1)–C(24)	102.1(10)
O(1)–Cu(1)–N(1)–C(11)	-118.0(15)
N(2)–Cu(1)–N(1)–C(11)	-22.3(11)
N(17)–Cu(1)–N(1)–C(11)	179.7(11)
O(2A)–Cu(1)–N(1)–C(11)	80.0(10)
O(1)–Cu(1)–N(1)–C(15)	57.6(18)
N(2)–Cu(1)–N(1)–C(15)	153.4(8)
N(17)–Cu(1)–N(1)–C(15)	-4.6(8)
O(2A)–Cu(1)–N(1)–C(15)	-104.3(8)
O(1)–Cu(1)–N(2)–C(2)	92(2)
N(1)–Cu(1)–N(2)–C(2)	-72(2)
N(17)–Cu(1)–N(2)–C(2)	0(3)
O(2A)–Cu(1)–N(2)–C(2)	-174(2)
Cu(1)–O(1)–C(24)–C(23)	-18.5(15)
Cu(1)–N(17)–C(18)–C(23)	-16.1(14)

The suffix "A" refers to atoms generated by the symmetry operation: *x*, -*y*+1/2, *z*+1/2.

of thiocyanate is found at 2118 cm⁻¹. The bands at 1591, 1482, 1435 cm⁻¹ for **1** are assigned to the pyridine skeleton.

The electronic spectra of copper(II) Schiff base complexes can be an indicator of metal centre geometry.²² The electronic spectrum of **1** in methanolic solution shows an absorption band in the region of 615 nm. It is assigned to a Cu(II) d–d transition and suggests five coordinated square pyramidal geometry.²³ The bands at 207 and 270 nm may be assigned to intraligand transitions.

Complex **1** obeys the Curie law over the 5–330 K temperature range due to the presence of copper(II) ion, and the plot of χ_MT versus T remains invariant. The χ_MT values of 0.48 and 0.11 cm³mol⁻¹K⁻¹ at 5 K and 330 K respectively, are typical for the one unpaired electron of the Cu(II) ion. These magnetic results indicate that moderate exchange interactions occur between the copper(II) ions.

At room temperature the solid-state ESR spectrum exhibits a very large intense peak along with a broad one. At 122 K four well-resolved anisotropic peaks are found with *g*_{||} = 2.136 and *g*_⊥ = 2.091, indicating the square-pyramidal geometry of the complex where *g*_{||} > *g*_⊥ and the unpaired electron is in the d_{x²-y²} orbital.

Experimental

Synthesis of 1: To a methanolic solution (25 ml) of the ligand L (2 mmol), Cu(NO₃)₂·6H₂O (0.597 g, 2 mmol) in a minimum amount of methanol was added. Then an aqueous solution (10 ml) of sodium thiocyanate (0.166 g, 2 mmol) was added dropwise and the resulting

mixture was kept at room temperature. After a few days, green crystals of **1** formed on slow evaporation of the solvent. Yield: 55%. Anal. found; C, 49.2; H, 2.8; N, 12.3; Cu, 18.5; calcd. for $C_{14}H_9CuN_3O_2S$: C, 48.9; H, 2.6; N, 12.1; Cu, 18.3 %.

Crystallographic data

A single crystal of **1** was covered in nujol and mounted with vacuum grease on glass fibre and intensity data were collected on a Bruker AXS P4 diffractometer with Mo-K α radiation (0.7107 Å) at 160 K, cooled with a Oxford Cryosystems Cryostream. No significant crystal decay was found. Data were corrected for absorption by ψ scans. The structures were solved by direct and different Fourier methods and refined by full-matrix least-squares on F^2 . Crystallographic computing was performed using the SHELXTL²⁴ programs. Further details are given in Table 1.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 205584. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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