Synthesis, crystal structure and magnetic properties of a polymeric copper(II) Schiff-base complex having binuclear units covalently linked by isonicotinate ligands

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The polynuclear copper(II) complex \([\text{Cu}_2 \text{L}(\text{O}_2 \text{CC}_5 \text{H}_4 \text{N})\cdot \text{C}_2 \text{H}_5 \text{OH}])_2\) (I), where \(\text{H}_2 \text{L}\) is a 1 : 2 Schiff base derived from 1,3-diaminopropan-2-ol and salicylaldehyde, has been prepared and structurally characterized. The structure consists of a one-dimensional zigzag chain in which the binuclear \([\text{Cu}_2 \text{L}]^2\) units are covalently linked by isonicotinate ligands to give a syndiatomic arrangement of the copper ions protruding outside the chain. In the basic unit, the copper(II) centres are bridged by an alkoxo and a carboxylato ligand, giving a Cu–Cu distance of 3.492(3) Å and a Cu–O–Cu angle of 130.9(2)°. While one copper centre has a square-planar geometry, the other copper is square-pyramidal with the pyridine nitrogen being the axial ligand. The visible electronic spectrum of \(\text{I}\) shows a Cu–O–Cu (φ) angle dependence on the sign and magnitude of the exchange parameter (−2J). A combination of carboxylato and hydroxo/alkoxo bridges gives asymmetrically dibridged complexes with a \([\text{Cu}_2 \mu-\text{X}]_2^2\) core (X = OH, OR, Cl) have been extensively studied.\\ The magnetostructural relationship for di-µ-hydroxo complexes shows a Cu–O–Cu (φ) angle dependence on the sign and magnitude of the exchange parameter (−2J). A combination of carboxylato and hydroxo/alkoxo bridges gives asymmetrically dibridged complexes with a \([\text{Cu}_2 \mu-\text{X}]_2^2\) core (X = OH, OR, Cl) have been extensively studied.\\ The present work stems from our interest in exploring the effect of covalently linking the asymmetrically dibridged dicopper(II) units into a one-dimensional chain on the superexchange interactions in a polymeric complex. The molecular unit chosen in the present study is an antiferromagnetically coupled \([\text{Cu}_2 \text{L}]^2\) moiety where the copper centres are bonded to a pentadentate Schiff-base \((\text{H}_2 \text{L})\) derived from 1 : 2 condensation of 1,3-diaminopropan-2-ol and salicylaldehyde. The binuclear units are covalently linked by isonicotinate ligands. Herein we present the synthesis, crystal structure and magnetic properties of \([\text{Cu}_2 \text{L}(\text{O}_2 \text{CC}_5 \text{H}_4 \text{N})\cdot \text{C}_2 \text{H}_5 \text{OH}])_2\) (I).

Experimental

Materials

All reagents and chemicals were purchased from commercial sources and used as received. The Schiff-base 1,3-bis(salicylidenediamine)-2-propanol (H₂L) was prepared by reacting 1,3-diaminopropan-2-ol (Fluka) with salicylaldehyde in a 1 : 2 molar ratio in an ethanolic medium and the solid was isolated on evaporation of the solvent. Copper(II) isonicotinate dihydrate was prepared by reacting copper(II) sulfate pentahydrate with sodium isonicotinate in water.\\ [Cu₂L(O₂CMe)] was prepared by following a reported procedure.

Synthesis of \([\text{Cu}_2 \text{L}(\text{O}_2 \text{CC}_5 \text{H}_4 \text{N})\cdot \text{C}_2 \text{H}_5 \text{OH}])_2\) (I)

The complex was prepared by following two different synthetic routes.

**Method 1.** 690 mg (ca. 2 mmol) of copper(II) isonicotinate dihydrate was refluxed for 5 min in 20 cm³ ethanol prior to the addition of 300 mg (ca. 1 mmol) of the Schiff-base \((\text{H}_2 \text{L})\) and 0.3 cm³ (ca. 3 mmol) of piperidine base in 15 cm³ ethanol. The mixture was refluxed for 6 h. The solution was cooled to ambient temperature, filtered and the filtrate, on slow evaporation, gave dark green crystalline blocks of \(\text{I}\) in ca. 75% yield.

**Method 2.** 480 mg (ca. 1 mmol) of \([\text{Cu}_2 \text{L}(\text{O}_2 \text{CMe})]\) was treated with 363 mg (ca. 2.5 mmol) of sodium isonicotinate in 30 cm³ ethanol and the solution was refluxed for 8 h. The reaction mixture was then cooled, filtered and the filtrate, on slow evaporation, gave crystalline blocks of \(\text{I}\) in ca. 80% yield. The product was separated, washed with cold ethanol and diethyl ether and finally dried in vacuo over \(\text{P}_2\text{O}_5\) (Found: C, 51.1; H, 4.3; N, 7.2. \(\text{C}_{28}\text{H}_{36}\text{N}_6\text{O}_4\text{Cu}_2\) (I) requires C, 50.8; H, 4.3; N, 7.1%).

Physical measurements

The elemental analysis was carried out using a Perkin-Elmer instrument. The visible electronic and EPR spectra were obtained with Hitachi U-3400 and Varian E-109 X-band spectrophotometers respectively. Variable-temperature magnetic susceptibility data in the temperature range 22–296 K were measured for a polycrystalline sample of \(\text{I}\) using a
George Associates Inc. Lewis-coil-force magnetometer system equipped with a closed-cycle cryostat (Air Products) working in the temperature range 20-300 K and a Cahm balance. Hg(CO)(NCS)₂] was used as a calibrant. Experimental susceptibility data were corrected for diamagnetic contributions (μ_m = 233.90 × 10⁻⁶ cm³ mol⁻¹) and temperature independent paramagnetism (N_v = 60 × 10⁻⁶ cm³ mol⁻¹ per copper atom). The magnetic moments at various temperatures were calculated in μ_B units [μ_B = 9.274 × 10⁻²⁴ J T⁻¹].

Crystal structure determination

Crystal data. C₆H₄Cu₃N₃O₇.M = 590.56, monoclinic space group P2₁/c (no. 14), a = 8.703 (3), b = 14.442 (3), c = 18.168 (12) Å, β = 93.214°, V = 2280(2) Å³, F(000) = 1208, Z = 4. D_x = 1.72 g/cm³, Cu-Kα radiation, λ = 1.5418 Å, μ(Cu-Kα) = 27.28 cm⁻¹, F = 294(2) K, transmission coefficients: 0.59–1.00.

Data collection and processing. Green crystalline blocks of composition [Cu₄L₂(O₂CCH₃)₃] · CH₃OH · H₂O, suitable for X-ray diffraction studies, were obtained by slow evaporation of an ethanolic solution of the polymeric complex. The intensity data were collected on an Enraf-Nonius CAD4 diffractometer with Cu-Kα radiation (1.5418 Å) using a crystal of approximate dimensions 0.30 × 0.15 × 0.13 mm. The data were corrected for Lorentz, polarization and absorption effects. A total of 4675 reflections were collected in the range 8° < 2θ < 150° by the ω–2θ scan technique of which 2921 reflections with I > 2σ(I) were used for the structure determination.

Structure solution and refinement. The structure was solved by the heavy-atom technique and subsequently by Fourier analyses. Besides the atoms belonging to the polymeric complex, there were three peaks in the difference-Fourier map with high electron density. These peaks were modeled for an ethanol solvent molecule. All non-hydrogen atoms were refined anisotropically. The hydrogens attached to the atoms in the complex were generated and assigned isotropic thermal parameters, riding on their parent atoms, and used for structure factor (F²) calculation only. The final full-matrix least-squares refinement converged to R = 0.0633 and wR = 0.1613 with a weighting scheme w = [σ²(F²) + (0.1028P)² + 4.48P]⁻¹ where P = [max(F², 0) + 2F²] / 3 using 325 parameters. All calculations were performed using PC-versions of the SHELXS-86 and SHELXL-93 programs.17 Atomic scattering factors were taken from ref. 18. The perspective view of the basic structural unit in the polymer was obtained using the ORTEP program.19 CCDC reference number 1861689.


Results and discussion

The polymeric complex 1 has been prepared in good yield from two different reactions. The reaction of copper(ii) isonicotinate dihydrate with the pentadentate ligand (L¹⁻) proceeds by dimerization of two monomeric units followed by polymer formation. The mechanistic pathways are not clear as the metal ion in copper(ii) isonicotinate is bonded to two pyridine nitrogens with the carboxylate moieties remaining uncoordinated.14 The reaction of [Cu₄L₄(O₂CMe)] with the sodium salt of isonicotinic acid leads to the formation of 1 through the substitution of acetate by the isonicotinate anion. The visible electronic spectrum of 1 in MeCN shows a broad band, centred at 615 nm (ε, 382 dm³ mol⁻¹ cm⁻¹) assignable to the d–d transition. The X-band powder EPR spectrum of the complex at 77 K shows a rhombic pattern giving g₁ = 2.19, g₂ = 2.06 and g₃ = 2.04.30

The crystal structure of 1 consists of a zigzag polymeric one-dimensional chain with the solvent molecules showing possible C–H · · · O hydrogen bonding interactions involving the imine

| Table 1 Selected bond lengths (Å), bond angles (°) and possible hydrogen bonding interactions in [Cu₄L₂(O₂CCH₃)₃] · CH₃OH · H₂O, (I) |
|---|---|---|---|
| Cu(1)–O(1)–Cu(2) | 2.19 | Cu(2)–O(2)–Cu(1) | 2.06 |
| Cu(1)–O(2)–Cu(1) | 2.06 | Cu(2)–O(3)–Cu(1) | 2.04 |
| Cu(1)–N(1)–Cu(2) | 1.98 | Cu(2)–N(2)–Cu(1) | 1.98 |
| Cu(1)–N(2)–Cu(2) | 1.98 | Cu(2)–N(3)–Cu(1) | 1.98 |
| Cu(1)–N(3)–Cu(2) | 1.98 | Cu(2)–O(4)–Cu(1) | 1.98 |
| Cu(1)–N(4)–Cu(2) | 1.98 | Cu(2)–O(5)–Cu(1) | 1.98 |
| Cu(1)–N(5)–Cu(2) | 1.98 | Cu(2)–O(6)–Cu(1) | 1.98 |
| Cu(1)–N(6)–Cu(2) | 1.98 | Cu(2)–O(7)–Cu(1) | 1.98 |

Symmetry operations: -x, y + 1/2, z - 1/2; x, y - 1/2, z + 1/2; x + 1, y + 1/2, z - 1/2.

carbons and one carbon of the pyridine ring. An ORTEP view of the basic structural unit of the chain is shown in Fig. 1. Selected bond distances and angles are given in Table 1. In

![Fig. 1 An ORTEP view of the binuclear structural unit in the polymeric complex [Cu₄L₂(O₂CCH₃)₃] · CH₃OH · H₂O, (I), showing the atom numbering scheme. The atom labeled as N(3) is related to N(3') by the symmetry operation -x, y + 1/2, z - 1/2.](image-url)
the binuclear unit, the copper atoms are bonded to the pentadentate Schiff-base and the isonicotinate ligands. The metal atoms are bridged by the alkoxide and the carboxylate oxygens. While Cu(1) has a 4 + 1 square-pyramidal geometry with a CuNO$_3$···N chromophore, the Cu(2) atom is bonded to one nitrogen and three oxygens forming a coordination plane. The deviations of Cu(1) from the O(1), O(2), O(5), N(1) plane and Cu(2) from the O(1), O(3), O(4), N(2) plane are 0.194(3) and 0.020(3) Å, respectively. The dihedral angle between the two copper containing planes is 19.0(3)$^\circ$. The Cu⋯Cu distance and Cu–O–Cu angle in I are 3.492(3) Å and 130.9(2)$^\circ$, respectively. In the basal planes, the average Cu–N distance is ca. 1.95 Å and the Cu–O distances are in the range 1.90 to 1.98 Å. The axial Cu–N distance is 2.411(6) Å. The Cu–O bonds involving the carboxylate are longer than the Cu–O phenolate and alkoxo bonds. The alkoxo oxygen has a planar geometry. The sum of the angles, viz. Cu(1)–O(1)–Cu(2), Cu(1)–O(1)–C(9) and Cu(2)–O(1)–C(9) is 353.5$^\circ$. A planar oxygen bridge is likely to favour an antiferromagnetic superexchange interaction between the two d$_{x^2-y^2}$ magnetic orbitals of the copper centres. The structural parameters in the dimeric unit of I are essentially similar to those reported in the discrete dicopper(II) complex [Cu$_2$L(O$_2$CPh)]H$_2$O, which has a Cu⋯Cu distance of 3.482(2) Å and a Cu–O–Cu angle of 132.7(3)$^\circ$.

The polymeric chain in I is shown in Fig. 2. The binuclear units are linked through axial ligation via the pyridine nitrogens of the isonicotinates, showing a μ$_1$ mode of bonding. The axial bonding results in the formation of a zigzag one-dimensional polymeric chain showing Cu(1)⋯Cu(1’) and Cu(2)⋯Cu(1’) distances of 9.283 and 9.124 Å, respectively. The polymeric chain consists of Cu(1) atoms with the Cu(2) atoms protruding out from the chain axis in a syndiotactic fashion (Fig. 2). The unit cell packing diagram shows a helical-type spatial arrangement of two polymer chains along the b axis (Fig. 3). The ethanol solvent molecules are involved in weak C–H⋯O hydrogen bonding interactions with the polymer chains (Table 1).

Variable temperature magnetic measurements show an increase in the susceptibility value on lowering the temperature in the range 296 to 22 K (Fig. 4). The $\mu_B$ value per copper atom decreases from 1.6 $\mu_B$ at 296 K to 1.34 $\mu_B$ at 39 K. Below this temperature it shows a marginal increase to 1.38 $\mu_B$ at 22 K. The overall magnetic behaviour of I is thus antiferromagnetic in nature. The magnetic chain system in I, shown in Fig. 5, can be modeled as an alternating-next-nearest-neighbour (ALNNN) linear chain system, described earlier by Hatfield and ter Haar for the CuH$_2$L$_2$(pht)$_2$ chain structure, where pht is a phthalate bridge. The Hamiltonian for such an ALNNN system can be written as

$$H = -2J\sum_{\sigma} S_{\sigma-1} S_{\sigma} - 2J'\sum_{\sigma} S_{\sigma-1} S_{\sigma+1}$$

$$S_{\sigma+1} = 2J\sum_{\sigma} S_{\sigma} S_{\sigma+1}$$

where $J$, $J_1$, and $J_2$ are the exchange coupling parameters resulting from the interactions in the dimeric core copper atoms Cu(1) and Cu(2); Cu(1) and Cu(1') interactions along the chain and interdimer intrachain interactions between Cu(1) and Cu(2). The Hamiltonian given by eqn. (1) is much too complicated for any closed form solutions. However, the conventional method of attack is to first diagonalize the Hamiltonian on the basis of states corresponding to finite chains. The infinite chain limits of these properties can be obtained by an appropriate extrapolation procedure.\(^\text{21,22}\) This, however, is a non-trivial exercise and is therefore not carried out here. Instead, various limiting cases have been tried for a theoretical fit of the susceptibility data.

In one limiting case, the polymeric complex is assumed to have strongly coupled binuclear units that are axially linked at the Cu(1) centre to form the one-dimensional chain. In such a case, where $J \gg J_1 = J_2$, the system should essentially behave as coupled dimeric units. The Hamiltonian of such an exchange coupled pair of atoms in an effective mean field can be obtained using Oguchi’s formula as

$$H = -2J_S^2S_0 - g_\mu_B(S_0 + S_\mu)H_e$$

where $H_e$ is the effective field acting on the dimeric unit due to the rest of the chain.\(^\text{24}\) The susceptibility equation for such a system can be expressed as

$$\chi = \frac{4N_\gamma^2\mu_B^2}{3kT}\left[\exp\left(-\frac{2JkT}{\theta}\right) - 3 \cdot 2J\right]$$

where $J$ is the exchange coupling within the dimer and $2J$ is the mean field exchange coefficient. The best fit obtained for eqn. (3) gives $J = 0$, $g = 2.1$, $\gamma = 255 \text{ cm}^{-1}$ with an $R$ value of 0.11 where $R = \frac{\chi_J}{\chi_{J_1}} = \frac{\chi_J}{\chi_{J_2}} = \frac{\chi_J}{\chi_{J_3}}$ (Fig. 4). This model fits well only for the data in the range 150 to 296 K and shows significant deviation at lower temperatures.

The magnetic behavior of 1 is significantly different from that of the discrete dimeric complex [Cu$_2$(L$_2$O$_2$CR)] (R = Me, Ph) which shows an antiferromagnetic interaction ($-2J \approx 170 \text{ cm}^{-1}$) and a Neel temperature of 170 K.\(^\text{11}\) Although the core structure of the basic unit of 1 is essentially similar to that of [Cu$_2$(L$_3$O$_2$CP)], the observed difference in the magnetic properties could be attributed to the presence of a polymeric chain having an extensive $\pi$-conjugation through the isonicotinate ligands. In such a situation, it can be assumed that the exchange interactions are equivalent ($J = J_1 = J_2$). As a consequence the exchange coupling interactions on the Cu(2) atom get effectively decoupled from the copper atoms belonging to the chain. This results in a system that consists of Cu(1) atoms belonging to the chain with an exchange constant of $J_1$ and an equal number of isolated Cu(2) centres showing Curie-type paramagnetic behaviour. The total susceptibility per copper can be expressed as:

$$\chi_t = \chi_{\text{chain}} + \chi_{\text{mono}}/2$$

where $\chi_{\text{mono}} = N g^2 \mu_B^2 / 4kT$. In the absence of any single ion anisotropy, the linear chain part can be modeled as a Heisenberg $S=1/2$ antiferromagnetic chain. To calculate the magnetic susceptibility of such a chain, a parameterized version of the Bonner–Fisher curves, derived by Torrance et al.,\(^\text{26}\) was used in the form

$$\chi_{\text{chain}} = (1.4892/J)[0.05031 + 0.013014x + 0.046846x^2 - 0.062319x^3 + 0.030834x^4 - 0.0076763x^5 + 0.0096332x^6 - 0.000048529x^7]$$

where $x = T/J$. The interaction between the chain and the monomeric units as well as the interchain interactions have been treated by a molecular field approximation.\(^\text{27}\) The expression for the corrected total susceptibility per copper atom is

$$\chi_t = \chi_t^{\text{corr}} = \chi_t / (1 - (2\gamma J/N g^2 \mu_B^2)^2)$$

The values of $\chi_t^{\text{corr}}$ gave an excellent theoretical fit to the experimental data giving $2J = -254 \text{ cm}^{-1}$, $g = 2.1$, $\gamma = 3 \text{ cm}^{-1}$ and $R = 7.823 \times 10^{-3}$, shown as line B in Fig. 4.

Finally, a mean field approach to the problem has also been considered. It is assumed that the Cu(1) and Cu(2) atoms form sublattices A and B, respectively. The effective fields at the sublattices are:

$$H_A = H_A + (4J + J_1)/N g^2 \mu_B^2 M_A + (4J_2)/N g^2 \mu_B^2 M_A,$$ $H_B = H_B + (J + J_2)/N g^2 \mu_B^2$$

These equations can be rewritten as: $H_A = H_A + 2\gamma M_A + 2\gamma M_A$ and $H_B = H_B + 2\gamma M_A$. In the high temperature limit ($g_\mu_B H / kT \ll 1$), the mean field equation takes the form

$$\chi = C(T - 0.5 \chi_T)$$

where $C = (N g^2 \mu_B^2 / 3kT)\left[\exp\left(-\frac{2JkT}{\theta}\right) - 3 \cdot 2J\right]$. The expression gives a good fit at high temperatures with $g = 2.1$, $\theta = -102 \text{ K}$ and $R = 5.6 \times 10^{-2}$. The value of $[J + J_1]$ is $-141.78 \text{ cm}^{-1}$. If we approximate $J = J_1 = J_2$, we get a $2J$ value of $-283.5 \text{ cm}^{-1}$ which is close to the value obtained from the other two models.

Considering all three models, it is apparent that the best theoretical fit in the entire temperature range is obtained from the one which considers complex 1 magnetically as an equi- molar mixture of copper atoms forming a linear Heisenberg chain and isolated Curie-type copper centres protruding outside the chain. This view is also supported by the possibility of frustration resulting from $J_1$ having the same sign as $J$ and $J_2$ (Fig. 5).

In summary, a new polymeric copper(II) complex [Cu$_2$(L$_2$O$_2$CC,H$_4$N)$_2$] in which the binuclear copper(II) units are covalently linked by isonicotinate to a one-dimensional zigzag chain has been prepared and structurally characterized. The complex is antiferromagnetic in nature. While the Cu(1) atoms lie along the chain, the Cu(2) atoms show a syndiatomic spatial arrangement. Although the binuclear unit in 1 has a structural similarity with its discrete dimeric analogue, the complexes differ considerably in their magnetic properties. These results are of significance for understanding the effect of polymerization on the magneto-structural properties of covalently linked asymmetrically bridged dicopper(II) complexes.

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