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A Ferromagnetically Coupled, Bent, Trinuclear Copper(II) Complex: Synthesis, Structure, Hydrogen-Bonding Network, Magnetic Properties and DNA Interaction Study

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A bent trinuclear copper(II) complex (**1**) incorporating μ-phenoxo, μ-*syn*-*syn* carboxylato, and μ_3-chloro bridges and an *O*,*N*,*N*-coordinated reduced Schiff-base ligand is reported. The complex shows an intramolecular ferromagnetic interaction in the solid state. The EPR spectra also support the magnetic behaviour of the complex. In the compound, each copper centre has a square-pyramidal geometry. The separation between the adjacent copper ions is about 3.05 Å and that between the terminal copper ions is about 5.0 Å. The complex forms a supramolecular architecture through N–H···Cl hydrogen bonding between the amine group of the reduced Schiff-base ligand and the counter chloride anions. Absorption and fluorescence spectral studies and viscosity measurements have been performed to determine the type of interaction with calf-thymus DNA. The nuclease activity of the complex with plasmid DNA is also studied.

Introduction

The chemistry of multinuclear copper complexes has aroused considerable interest in recent years as copper has been found in the active sites of a large number of metalloproteins[1,2] as well as because of their interesting magnetic properties.[3] Among the multicentred copper proteins, the active sites of particulate methane monooxygenase (pMMO),[4] laccase[5] and ascorbate oxidase[6] contain trinuclear copper(II) sub-units. It has been documented that trinuclear copper(II) centres exhibit the $S = 3/2$ ground state in the fully oxidised form of pMMO.[7] It is also reported that the oxidised form of the active site of ascorbate oxidase consists of an angled trinuclear copper(II) moiety with a Cu···Cu separation in the range 3.66–3.90 Å, with appropriate C_2 symmetry.[6] Although a few ferromagnetically coupled trinuclear copper(II) complexes have been reported,[8,9] to the best of our knowledge studies on mixed-bridged bent trinuclear copper(II) complexes are rare.[10] Thus, there is an increasing demand for mixed-bridged angular trinuclear copper(II) systems in order to better understand the underlying chemistry as well as the magnetic properties of biomolecules. Furthermore, the studies of such systems may be helpful in order to develop the fundamental knowledge about the exchange interactions between the paramagnetic centres of such systems and in the design of molecular-based ferromagnetic materials. These considerations have generated a lot of interest in the synthesis and characterisation of ferromagnetically coupled mixed-bridge bent trinuclear copper(II) complexes using conformationally labile reduced Schiff-base ligands.

The study of the interaction of polynuclear copper(II) complexes with DNA and their nuclease activity is also of abiding interest in the field of bioinorganic chemistry of copper.[11] This is because such polynuclear complexes might interact with DNA by different pathways and exhibit DNA cleavage activity.[8a,12] Thus, developments in the field of DNA interaction and cleavage studies with small molecules have prompted us to explore the binding of trinuclear copper(II) complexes with DNA and their nuclease activity.

Besides the importance of understanding the chemistry, magnetic properties and DNA interaction studies with biologically related polynuclear copper(II) complexes, the design of polynuclear coordination clusters by self-assembly of small building blocks has also received a great deal of attention in the context of crystal engineering, molecular recognition and supramolecular chemistry.[13–15] One particularly interesting method in the construction of self-assembled clusters involves using a ligand that can be involved in coordination and hydrogen-bonding interactions simultaneously, such that the transition metal cationic centres are linked through anions by hydrogen bonding to form a self-assembled cluster. Reduced Schiff-base ligands

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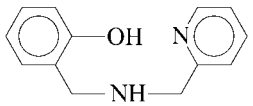
have great potential in the organisation of the primary molecule in the solid state by intermolecular hydrogen bonding.[16] This has also motivated us to undertake the task of designing a supramolecular cluster in the solid state by self-assembly with bifunctional reduced Schiff-base ligands.

Here we describe the synthesis of a mixed-bridge (μ-phenoxo, μ-carboxylato, and μ_3-chloro) trinuclear copper(II) complex incorporating an *O*,*N*,*N*-coordinated reduced Schiff-base ligand. The X-ray structure of the complex has been determined, which allows the secondary interactions in the solid state to be investigated thoroughly. Variable temperature magnetic susceptibility measurements confirm the ferromagnetic behaviour, and the EPR spectra also support the magnetic behaviour. The solution properties are studied, and the interaction with DNA and nuclease activity of the complex is scrutinized.

Results and Discussion

The reduced Schiff base ligand (**HL**) used in this work was prepared by $NaBH_4$ reduction of the corresponding Schiff base in methanol.[17]



HL

The stoichiometric reaction of copper(II) chloride dihydrate with **HL** and benzoic acid in the presence of piperazine in methanol afforded a dark coloured complex of formula $[Cu_3L_2(C_6H_5COO)_2Cl]Cl$ in good yield. This complex displays carboxylate stretches near 1560 and 1420 cm^{-1}, respectively. The splitting between the two peaks is 140 cm^{-1}, which indicates that the carboxylate group bridges the two copper ions in a *syn-syn* fashion.[18] The band at around 1200 cm^{-1} is assigned to the $\nu(C–O_{phenolate})$ vibration. The hydrogen-bonded NH vibration occurs as a broad band near 3400 cm^{-1}.

The electronic spectra were recorded in Tris-HCl/NaCl buffer solution; the data are summarised in the Exp. Sect. The complex exhibits a single d-d absorption band near 650 nm which is characteristic of square-pyramidal copper(II) complexes.[19] The allowed intense band observed near 420 nm is believed to be due to an LMCT transition between bridging phenoxide and copper(II) ions.[19]

Molecular Structure

The crystal structure of $[Cu_3L_2(C_6H_5COO)_2Cl]Cl$ (**1**) was determined. The asymmetric unit consists of one half of a centrosymmetric molecule; Figure 1 shows the cationic part of the molecular structure and the bond parameters are listed in Table 1.

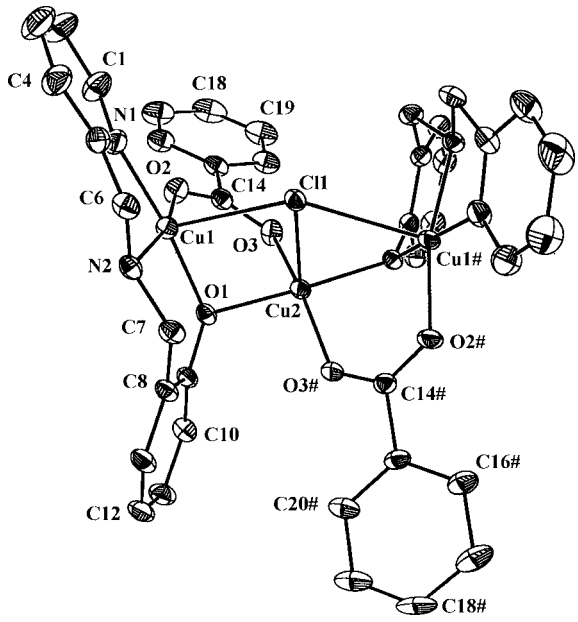


Figure 1. Perspective view and atom-labelling scheme for the cationic part of $[Cu_3L_2(C_6H_5COO)_2Cl]Cl$ (**1**). All non-hydrogen atoms are represented by 30% thermal probability ellipsoids.

Table 1. Selected bond lengths [Å] and angles [°] for $[Cu_3L_2(C_6H_5COO)_2Cl]Cl$.

Cu(1)–N(2)	1.981(4)
Cu(1)–O(1)#	1.947(3)
Cu(1)–O(2)	1.929(3)
Cu(1)–Cl(1)	2.732(2)
Cu(2)–O(1)	1.973(3)
Cu(2)–O(3)	1.926(4)
Cu(2)–Cl(1)	2.654(2)
Cu(1)···Cu(2)	3.055(8)
Cu(1)···Cu(1)#	5.104(8)
N(1)–Cu(1)–N(2)	82.00(19)
N(1)–Cu(1)–O(1)#	173.79(16)
N(1)–Cu(1)–O(2)	91.40(18)
N(1)–Cu(1)–Cl(1)	98.74(15)
N(2)–Cu(1)–O(1)#	94.14(16)
N(2)–Cu(1)–O(2)	165.73(18)
N(2)–Cu(1)–Cl(1)	91.22(14)
O(1)#–Cu(1)–O(2)	91.28(15)
O(1)#–Cu(1)–Cl(1)	86.16(10)
O(2)–Cu(1)–Cl(1)	102.32(12)
O(1)–Cu(2)–O(1)#	175.67(19)
O(1)–Cu(2)–O(3)	90.10(14)
O(1)–Cu(2)–O(3)#	90.70(14)
O(1)–Cu(2)–Cl(1)	87.83(10)
O(3)–Cu(2)–O(3)#	159.0(3)
O(3)–Cu(2)–Cl(1)	100.50(13)
Cu(1)#–O(1)–Cu(2)	102.40(14)
Cu(1)–Cl(1)–Cu(2)	69.10(3)
Cu(1)–Cl(1)–Cu(1)#	138.20(7)
Cu(1)–Cu(2)–Cu(1)#	113.31(3)

Symmetry operation for Cu(1)#, O(1)# and O(3)#: 2/3 + *x*, –2/3 + *y*, 1/6 – *z*.

The compound possesses a twofold axis through the central copper atom. In the cationic part, the adjacent copper atoms are bridged by the phenoxy oxygen atom of the deprotonated ligand L and two oxygen atoms of a didentate

syn-syn benzoato group to give a bent trinuclear entity. The three copper atoms in the trinuclear moiety form an isosceles triangle with an adjacent Cu···Cu distance of 3.055(8) Å and a terminal Cu···Cu distance of 5.104(8) Å. The Cu(1)–Cu(2)–Cu(1)# and Cu–$O_{phenoxo}$–Cu angles are 113.31(3)° and 102.40(14)°, respectively. The geometry of each copper ion is distorted square-pyramidal in which the basal plane of the terminal copper atoms consists of two nitrogen (pyridine and amine) and two oxygen (phenoxo and benzoato) atoms while that of the central copper atom contains four oxygen atoms. The equatorial planes are essentially planar (mean deviation = 0.0649 and 0.2128 Å) and the dihedral angle between the terminal and central basal planes is 65.7°. The apical site of each copper ion is occupied by the μ_3-chloro group. The Cu–(μ_3-Cl) bond lengths span the range 2.654(2) to 2.732(2) Å and are significantly larger than the terminal Cu–Cl bond. Cu(1) is displaced by 0.1550 Å whereas Cu(2) is shifted by 0.1381 Å towards the apical chloride group. The Cu–N and Cu–O bond lengths are normal.

Hydrogen Bonding

The primary structure of the compound is remarkably different from its solid-state structure due to the involvement of secondary interactions in the lattice. In the extended solid-state structure a self-assembled cluster compound is formed by simultaneous coordinative and hydrogen-bonding interactions. The amine hydrogen atom of both the reduced Schiff-base ligands in the trinuclear entity engage in hydrogen bonding. The chloride ion is symmetrically hydrogen bonded with the amine hydrogen atom [Cl···N = 3.163(6) Å] of one of the reduced Schiff-base ligands of three different molecules. The basic unit of the cluster is shown in Figure 2. The remaining three amine hydrogen atoms of the three different molecules of the small building blocks are anchored within an extended hydrogen-bonding network. This interaction leads to the formation of macrocyclic cavities with six molecules of average diameter 25.0 Å; the hydrogen-bonded macrocyclic cavity is shown in Figure 3. The hexameric synthons are again assembled in the crystal lattice through similar types of intermolecular contacts to form a honeycomb-like supramolecular array. This honeycomb network is shown in Figure 4.

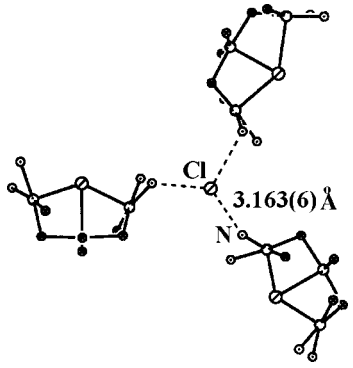


Figure 2. Basic unit of secondary interactions of $[Cu_3L_2(C_6H_5COO)_2Cl]Cl$ (**1**); carbon and hydrogen atoms have been excluded for clarity.

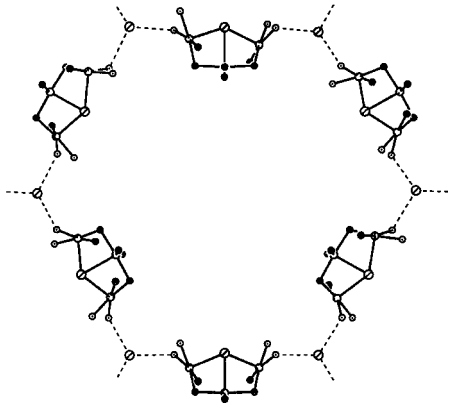


Figure 3. Hexameric macrocycle of **1**; carbon and hydrogen atoms have been excluded for clarity.

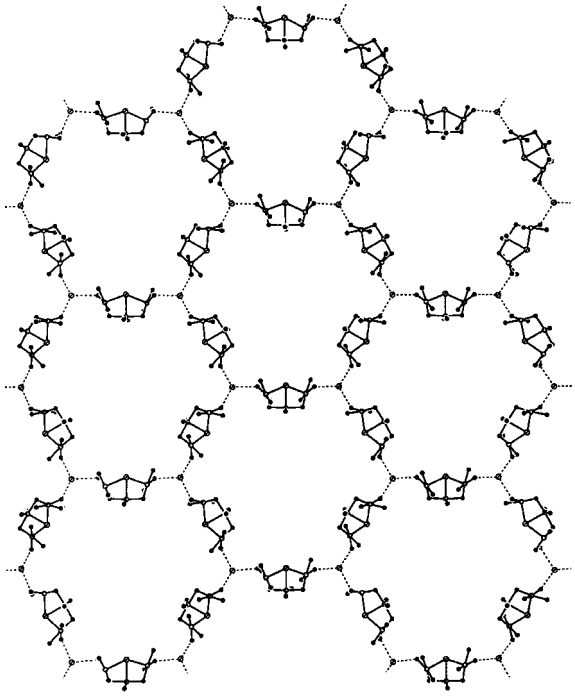


Figure 4. Supramolecular network in the lattice of **1**; carbon and hydrogen atoms have been excluded for clarity.

Magnetic Studies

The variable-temperature magnetic susceptibility, χ_M, per trinuclear copper(II) unit was measured in the temperature range 2–300 K. A $\chi_M T$ value of 1.32 $cm^3 mol^{-1} K$ is observed for **1** at 300 K, which is as expected for three magnetically quasi-isolated spin doublets ($g > 2.00$). Upon decreasing the temperature the $\chi_M T$ value increased to 1.87 $cm^3 mol^{-1} K$ at 7 K. Such magnetic behaviour is characteristic of a predominant ferromagnetic exchange coupling in a trinuclear copper(II) system. The plot of $\chi_M T$ vs.

T is given in Figure 5. After passing through the maximum, the $\chi_M T$ value decreases quickly to 1.60 $cm^3 mol^{-1} K$ at 2 K. The magnetic orbitals of the terminal copper ions in **1** have predominantly $d_{x^2-y^2}$ character. A significant exchange interaction between two terminal copper atoms through the bridging chloride ligand may be excluded in the isolated trinuclear moiety because the delocalisation of an unpaired electron towards the apical chloride ion is likely to be less effective due to the large Cu–(μ_3-Cl) bond length.[20] The decrease of $\chi_M T$ at low temperature is probably either due to a zero-field splitting effect (D parameter) for the $S = 3/2$ ground state or inter-cluster antiferromagnetic interactions (J'). Both D and J' exhibit the same behaviour in the low-temperature regime. However, in the case of copper(II), the possible D parameters of the $S = 3/2$ ground state must be very small due only to the dipolar interactions. Therefore, for simplification, the D parameter was not taken into consideration when fitting the experimental data. The fit of the susceptibility data was carried out using the molecular field approximation, with the J' parameter, according to the method given by Kahn,[3] with the Hamiltonian

$$H = -J(S_1S_2 + S_2S_3) + g\beta H\mathbf{S}_z - zJ'\langle\mathbf{S}_z\rangle\mathbf{S}_z$$

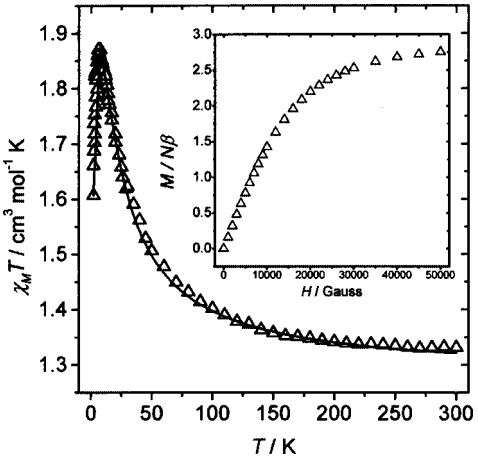


Figure 5. Plot of $\chi_M T$ vs. T for $[Cu_3L_2(C_6H_5COO)_2Cl]Cl$ (**1**) (open points are the experimental data and the solid line represents the best fit obtained). Plot of the reduced magnetisation, $M/N\beta$, vs. H for **1** at 2 K (see inset).

With this molecular field approach (neglecting D parameter), the best-fit parameters for complex **1** are: $J = 20.8 \pm 0.2$ cm^{-1}, $J' = -0.4 \pm 0.2$ cm^{-1}, $g = 2.13 \pm 0.01$ and $R = 1.2 \times 10^{-4}$ [$R = \Sigma(\chi_M^{calc} - \chi_M^{obs})^2/\Sigma(\chi_M^{obs})^2$].

The nature of the reduced molar magnetisation is shown in the inset of Figure 5. The $M/N\beta$ value at 5 T is close to $3N\beta$ and this value indicates the tendency to have three unpaired electrons ($S = 3/2$) at 2 K.

The ferromagnetic interaction in the present complex can be explained by considering the dihedral angle between the equatorial planes of the terminal and central copper(II) centres.[21] It is known that spin coupling between the paramagnetic centres becomes ferromagnetic when the dihedral angle decreases from 180°. In complex **1** the dihedral angle of 65.7° deviates significantly from the value of 180°. These results also support the ferromagnetic interactions.

EPR Spectra

Variable-temperature EPR spectra of the complex were recorded to find out more about the behaviour of the unpaired electron within the trinuclear cluster in the solid state. The X-band EPR spectra of polycrystalline powdered complex at different temperatures are shown in Figure 6.

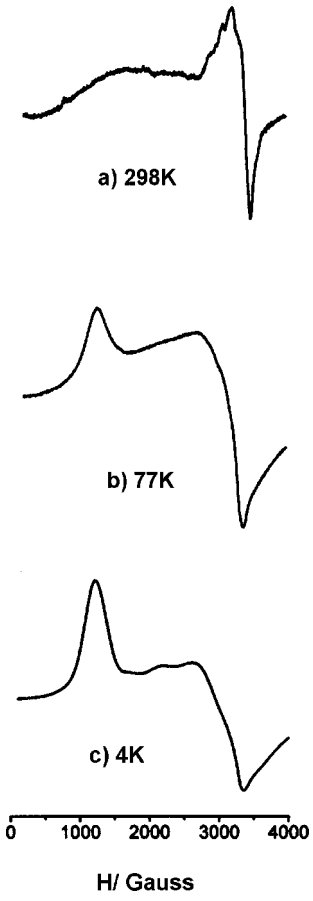


Figure 6. Solid powder X-band EPR spectra of $[Cu_3L_2(C_6H_5COO)_2Cl]Cl$ (**1**).

The EPR spectrum at 4 K is dominated by a transition at 1215 G (Figure 6, c), which unambiguously identifies the $S = 3/2$ ground spin-state. At this temperature the signals within the ±1/2 and ±3/2 Kramer's doublets are observed. It is clear from the variable-temperature studies (Figure 6) that the intensity of the $M_S = \pm 1/2$ EPR spectra increases with decreasing temperature. At 4 K the effective $g_\perp$ value is found at 5.2; this value may arise due to the transition within $M_S = \pm 1/2$ of the Kramer doublet of quadruplets state ($S = 3/2$). The corresponding $g_\parallel$ value is observed at 2.15. It is interesting to note that the strong signal at low field gradually broadens and almost disappears with increasing temperature (Figure 6). However, the signal corresponding to $g \approx 2.0$ remains almost unchanged. These

spectral features have been attributed to the increasing population of the two $S = 1/2$ excited states with a rise in temperature. As a consequence, there is compensation of the $S = 3/2$ ground state and the room-temperature spectrum is more reminiscent of the $S = 1/2$ term. All the spectral observations are in good agreement with the magnetic moment of the complex.

Interaction Between DNA and the Complex

Electronic absorption spectroscopic techniques are often employed to investigate the binding of DNA with complexes. To achieve this, the absorption spectra of the complex in the absence and presence of calf-thymus DNA at different concentrations were measured. The UV/Vis spectral change with increasing DNA concentration for **1** is shown in Figure 7. A considerable hypochromicity without appreciable change in wavelength of the d-d and charge-transfer transitions can be attributed to an interaction[22] between the surface of the DNA molecule and the trinuclear complex. The binding constant between DNA and the complex was determined from the UV/Vis spectroscopic data using the following equation[23]

$$[DNA]/(\varepsilon_a - \varepsilon_f) = [DNA]/(\varepsilon_b - \varepsilon_f) + 1/K_b(\varepsilon_a - \varepsilon_f)$$

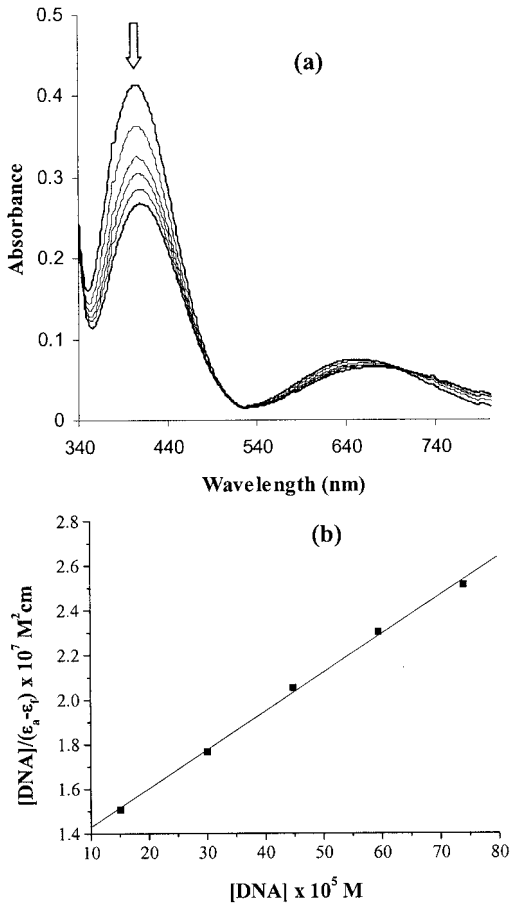


Figure 7. (a) Absorption spectra of $[Cu_3L_2(C_6H_5COO)_2Cl]Cl$ (**1**) in 50 mM Tris-HCl and 18 mM NaCl buffer (pH 7.2) in the presence of increasing amounts of DNA ([DNA] = 0–75 μM). (b) Plot of $[DNA]/(\varepsilon_a - \varepsilon_f)$ vs.[DNA].

where ε_a, ε_f and ε_b correspond to $A_{obs.}/[Cu]$, the extinction coefficient of the free copper complex and the extinction coefficient of the copper complex in the fully bound form, respectively. The binding constant obtained is 1.38×10^5 M^{-1}.

Fluorescence spectra of the ethidium bromide–DNA intercalative adduct were recorded in the presence of the complex. No considerable quenching of fluorescence intensity was observed in the presence of **1**, which suggests that there is no significant intercalation between DNA and the metal complex.

Viscosity measurement is an important tool to ascertain the interaction mode[24] of DNA with complexes. It has been established that a significant enhancement in viscosity of a DNA solution is observed in the case of classical intercalative binding of complexes.[25] However, groove-face, electrostatic or surface binding of the compounds results in less or no change of viscosity of the DNA solution.[26] The η/η_0 values are given in Table 2. The results show that there is a slight decrease in relative viscosity of calf-thymus DNA solution in the presence of this trinuclear complex and this is probably due to interaction of the complex with the DNA surface.

Table 2. Data for DNA viscosity in the presence of complex **1**.

[complex]/[DNA][a]	η/η_0
0.0	1.00
0.13	0.992
0.17	1.002
0.22	0.990
0.26	0.971
0.31	0.952
0.35	0.950

[a] [DNA] = 200 μM.

In summary, the UV/Vis spectral, fluorescence and viscosity measurements reveal that the trinuclear complex interacts with the DNA surface and is inhibited from intercalation with the DNA molecule. This interaction mode is different from that of previously reported trinuclear copper species.[8a]

Cleavage of pUC18 DNA by $[Cu_3L_2(C_6H_5COO)_2Cl]Cl$ (1)

The cleavage of supercoiled pUC18 DNA by the complex was studied by gel electrophoresis in Tris-HCl/NaCl buffer. Figure 8 shows the gel electrophoresis separation of plasmid DNA induced by our mixed-bridge, bent, trinuclear copper(II) complex. From this figure it can be seen (lane 5) that the complex itself converts plasmid supercoiled pUC18 DNA into a mixture of supercoiled (Form I) and nicked (Form II). The activity increases remarkably in the presence of H_2O_2 (lane 6). However, there is no significant increase (lane 7) in the conversion on addition of 2-mercaptoethanol to the complex and H_2O_2. Incubation with H_2O_2, 2-mercaptoethanol or both H_2O_2 and 2-mercaptoethanol without the complex does not cause strand scission of supercoiled DNA. These experimental results demonstrate that complex **1** exhibits DNA cleavage activity that is enhanced by the addition of hydrogen peroxide. We assume that there is a

possibility of formation of copper-oxo species during the DNA cleavage reaction in the absence or presence of H_2O_2.[27] This copper species is probably responsible for the cleavage of DNA by the trinuclear complex alone (lane 5). Besides the copper-oxygen species, the generation of hydroxy radicals in the presence of H_2O_2 enhances the DNA cleavage activity (lane 6).[27]

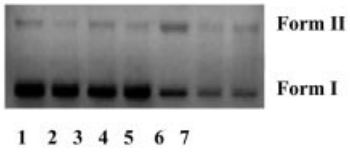


Figure 8. Electrophoretic separation of pUC18 DNA by $[Cu_3L_2(C_6H_5COO)_2Cl]Cl$ (**1**). DNA alone (lane 1), DNA + 2-mercaptoethanol (lane 2), DNA + H_2O_2 (lane 3), DNA + H_2O_2 + 2-mercaptoethanol (lane 4), DNA + **1** (lane 5), DNA + **1** + 100 μM H_2O_2 (lane 6), DNA + **1** + H_2O_2 + 2-mercaptoethanol (lane 7).

Conclusions

A conformationally labile reduced Schiff-base ligand having coordinating and hydrogen-bonding sites has been successfully utilized to synthesise a phenoxo, carboxylato, chloro-bridged bent trinuclear copper(II) complex in good yields. The separations between the copper ions in the complex fall in the range 3.05–5.10 Å, which is in agreement with the trinuclear active sites of the oxidized form of ascorbate oxidase.[6] The ferromagnetic behaviour of the complex also resembles the oxidized form of particulate methane monooxygenase.[7] The variable-temperature EPR spectral measurements support the magnetic behaviour. Spectral and viscosity measurements reveal the surface binding of **1** to calf thymus DNA. Cleavage of pUC18 by **1** indicates that the complex exhibits nuclease activity. Interesting supramolecular structures are obtained in the solid state through the combination of hydrogen bonding between the chloride ion and the NH group of the reduced Schiff-base ligand. The results presented herein may be helpful in understanding the chemistry and magnetic properties of biomolecules containing trinuclear sub-units in their active sites. In addition, the studies also provide valuable insights into the synthesis of supramolecules by self-assembly of reduced Schiff-base ligands. Further research aimed at the synthesis of polynuclear mixed-bridged copper complexes containing different reduced Schiff-base ligands, investigation of their DNA interaction and clarification of the cleavage mechanism, along with their solid- and solution-state behaviour is currently in progress.

Experimental Section

Materials: All the starting chemicals were analytically pure and were used without further purification. The ligand was prepared by reduction of the corresponding Schiff base derived from salicylaldehyde and 2-(aminomethyl)pyridine with $NaBH_4$.[17] Calf thymus (CT) DNA and supercoiled pUC18 DNA were obtained from Sigma. The concentration of calf thymus DNA (200 μM) was estimated spectrophotometrically from the extinction coefficient of DNA (6600 $M^{-1}cm^{-1}$) at 260 nm.[28] Agarose (molecular biology grade), 2-mercaptoethanol, and ethidium bromide were purchased from Sigma.

Physical Measurements: UV/Vis spectra were recorded with a Perkin–Elmer LAMBDA25 spectrophotometer and IR spectra were measured with a Perkin–Elmer L-0100 spectrometer. Electrochemical measurements were performed (acetonitrile solution) with a CH620A electrochemical analyzer using a platinum electrode. Tetraethylammonium perchlorate (TEAP)[29] was used as supporting electrolyte and the potentials are referenced to the standard calomel electrode (SCE) without junction correction. EPR spectra were recorded with a Bruker 300E automatic spectrometer, varying the temperature between 4–300 K. Magnetic measurements were carried out on polycrystalline samples with a Quantum Design MPMS XL SQUID susceptometer operating at a magnetic field of 0.1 T between 2 and 300 K. The diamagnetic corrections were evaluated from Pascal's constants. Elemental analyses (C, H, N) were performed with a Perkin–Elmer 2400 Series II elemental analyzer.
Viscosity measurements were performed with an Ubbelohde viscometer at 27 ± 0.1 °C. The concentration of DNA was 200 μM. The flow times were determined with a digital stop clock and each measured point is the average of four readings. Viscosity values are presented as η/η_0 vs. [complex]/[DNA], where η is the viscosity of DNA in the presence of complex and η_0 is the viscosity of DNA solution alone.
The gel electrophoresis experiments were performed by incubation at 37 °C for 1 h as follows: pUC18 DNA (200 ng), complex (40 μM), H_2O_2 (100 μM), and 2-mercaptoethanol (100 μM) in 50 mM Tris-HCl/18 mM NaCl buffer (pH 7.2). The sample was electrophoresed for 2 h at 40 V on 1% agarose gel using Tris-boric acid-EDTA buffer (pH 8.3). After electrophoresis, the gel was stained using 1 μg mL ethidium bromide and photographed under UV light.

$[Cu_3L_2(C_6H_5COO)_2Cl]Cl$ (1): A methanolic solution (5 mL) of benzoic acid (70 mg, 0.6 mmol) containing piperazine (45 mg) was added to a solution of $CuCl_2{\cdot}2H_2O$ (90 mg, 0.6 mmol) in methanol (15 mL). A methanolic solution of **HL** (107 mg, 0.5 mmol) was added to the resulting solution. Slow evaporation of the dark-green solution yielded a dark-green crystalline product. Yield: 70% (340 mg). $C_{40}H_{34}Cl_2Cu_3N_4O_6$ (927.5): calcd. C 51.75, H 3.67, N 6.04; found C 51.4, H 3.4, N 5.9 ppm. IR (KBr): ν(C–$O_{phenolate}$) 1240; ν(COO^-) 1420, 1560; ν(NH) 3400 cm^{-1}. UV/Vis [Tris-HCl/NaCl buffer]: λ_{max} (ε) = 650 nm (1480 $M^{-1}cm^{-1}$), 420 (8260). E_{pa} ($Cu_3^{II}/Cu_2^{II}Cu^{III}$ couple): 1.1 V (irr); E_{pc} ($Cu_3^{II}/Cu_2^{II}Cu^{I}$ couple): –0.5 V (irr).

Crystallographic Studies: Suitable crystals of complex **1** were grown by slow evaporation of a methanolic solution. The X-ray intensity data were measured at 293 K with a Bruker AXS SMART APEX CCD diffractometer (Mo-K_α, λ = 0.71073 Å). The detector was placed at a distance of 6.03 cm from the crystal. A total of 606 frames were collected with a scan width of 0.3° in different settings of φ. The data were reduced with SAINTPLUS[30] and an empirical absorption correction was applied using the SADABS package.[30] Metal atoms were located by direct methods and the rest of the non-hydrogen atoms emerged from successive Fourier synthesis. The structure was refined by full-matrix least-square procedures on F^2. All non-hydrogen atoms were refined anisotropically. The amine hydrogen atoms were located directly in the difference Fourier maps and the remaining hydrogen atoms were included in calculated positions. Calculations were performed with the SHELXTL V5.03[31] program package. Relevant crystal data are given in Table 3.

Table 3. Crystallographic data for **1**.

Formula	$C_{40}H_{34}Cl_2Cu_3N_4O_6$
M_w	927.5
Space group	*R*-3*c*
a [Å]	21.773(3)
b [Å]	21.773(3)
c [Å]	51.579(8)
α [°]	90
β [°]	90
γ [°]	120
V [Å^3]	21176.0(5)
Z	21
T [K]	293(2)
$\rho_{calcd.}$ [mg m^{-3}]	1.311
μ (Mo-K_α) [mm^{-1}]	1.483
*R*1,[a] *wR*2[b] [$I > 2\sigma(I)$]	0.0654, 0.1909

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

CCDC-275218 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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