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LETTER

Azide-bridged dinuclear copper(II) complexes with various chelate ring sizes: diamagnetic model complex for type III copper protein

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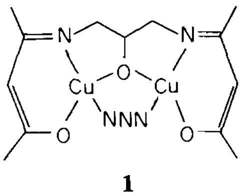
The relationship between structure and physical properties such as magnetism and spectroscopy in type III copper proteins is a subject of considerable importance. In connection with these studies, the diamagnetic metazidohemocyanin (metHc(N_3)) have been chemically prepared by the addition of azide ion to hemocyanins from American whelk and horseshoe crab [1, 2]. The dinuclear copper active site of metHc(N_3) has been proposed to include an exogenous azide ion, which links in μ-1,3-fashion between two copper(II) ions [1, 2]. The μ-azide-μ-phenoxy dinuclear copper(II) complexes have been prepared as models for the active site of type III copper proteins [3]. However, to our knowledge, there have been only a few papers published on the preparation and characterization of the dinuclear copper(II) complexes bridged by both alkoxide oxygen and azide nitrogen [4, 5]. In this paper, we report the synthesis and magnetic properties of μ-azide-μ-alkoxo dinuclear copper(II) complexes **1** and **2** containing Schiff bases derived from acetylacetone and 1,3-diamino-2-propanol or 1,5-diamino-3-pentanol.



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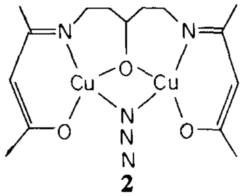

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The Schiff bases L_1 and L_2 were obtained by the reaction of acetylacetone with 1,3-diamino-2-propanol and 1,5-diamino-3-pentanol, respectively [6, 7]. Complex **1** was prepared by stirring the mixture of Schiff base L_1 (0.38 g, 1.5 mmol), $Cu(ClO_4)_2 \cdot 6H_2O$ (1.11 g, 3.0 mmol), NaN_3 (0.098 g, 1.5 mmol) and NaOH (0.18 g, 4.5 mmol) in ethanol solution. A similar method was also applied for the synthesis of complex **2**. Complex **1**: dark purple crystals. *Anal.* Found: C, 36.99; H, 4.46; N, 16.45. Calc. for $[Cu_2(C_{13}H_{19}N_2O_3)(N_3)]$: C, 37.13; H, 4.56; N, 16.66%. Complex **2**: dark brown crystals. *Anal.* Found: C, 40.02; H, 5.09; N, 15.76. Calc. for $[Cu_2(C_{15}H_{23}N_2O_3)(N_3)]$: C, 40.16; H, 5.18; N, 15.62%.

The IR spectrum of **1** shows $\nu_{asym}(N_3^-)$ absorption at 2020 cm^{-1}, indicating that an azide ion links two copper(II) ions in μ-1,3-fashion as given in the structural formula [8]. On the other hand, a μ-1,1-azide bridge is expected for **2** ($\nu_{asym}(N_3^-)$: 2100 cm^{-1}) [8]. The magnetic moment (μ_{eff}) for **1** and **2** gave 0.20 and 1.46 BM at room temperature, respectively. From temperature-dependence magnetic susceptibility measurement, complex **1** is diamagnetic in the temperature range 77–300 K. Furthermore, this complex is ESR-silent in solid and chloroform solution. Figure 1 represents the temperature-dependence of the magnetic susceptibility for complex **2**. This complex exhibits antiferromagnetic interaction ($2J = -252$ cm^{-1}) that is much weaker than that observed for **1**. In azide-bridged dinuclear copper(II) complexes, the strength of antiferromagnetic coupling between two copper(II) ions is dependent on the geometry around copper(II) and the bridging mode of the azide ion [4, 6, 8–11]. Perhaps the diamagnetism of **1** is attributable to the fact that the two copper(II) basal planes are nearly

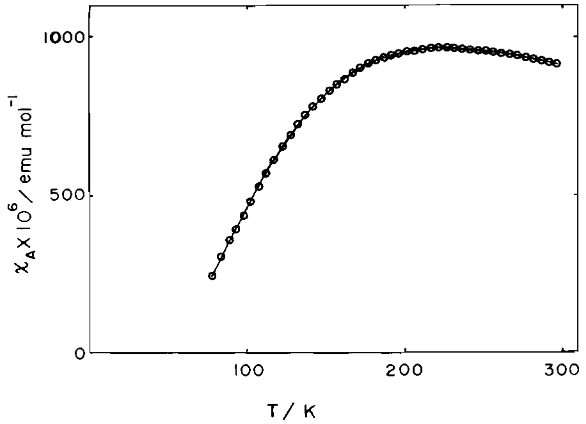

Fig. 1. The temperature-dependence of magnetic susceptibility of complex **2**. The solid line shows theoretical susceptibility calculated by the Bleaney–Bowers equation with $g = 2.08$, $J = -126$ cm^{-1} and $N\alpha = 60 \times 10^{-6}$ cgs emu mol^{-1}.

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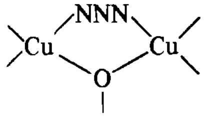
coplanar and an azide ion bridges two copper(II) ions in a 1,3-fashion. Thus, we consider that the coplanality of the bridging group



is attained in metHc(N_3) [1, 2]. In this case, it is considered that the oxygen atom from OH^- or O^{2-} instead of alkoxide bridges two copper(II) ions [12]. The color of the chloroform solution is purple for **1** and green–brown for **2**. The electronic spectra of the chloroform solutions showed that λ_{max} of **1** are 553 (ϵ, 810 M^{-1} cm^{-1}) and 352 nm (ϵ, 4610 M^{-1} cm^{-1}), and those of **2** are 565 (ϵ, 96 M^{-1} cm^{-1}) and 436 nm (ϵ, 1600 M^{-1} cm^{-1}). These data show that a visible absorption band in **1** has a very large ϵ value, which is close to those of metHc(N_3) ($\epsilon \sim 600$ M^{-1} cm^{-1} at $\lambda_{max} \sim 500$ nm [13]).

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