Synthesis, crystal structure and magnetic properties of the first dinuclear copper(II)–iron(II) complex [Cu(L)Fe(CN)₅NO] based on nitroprusside

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Abstract
The nitrosyl cyanide [Cu(L)Fe(CN)₅NO] was prepared by the reaction of [Cu(L)]Cl₂ [L = 3, 10-bis(2-hydroxy-methyl)-1,3,5,8,10,12-hexaazacyclotetradecane] with Na₂[Fe(CN)₅NO]Æ2H₂O in aqueous solution. Single-crystal analysis revealed that the title complex is the first structurally characterized dinuclear copper(II)–iron(II) complex based on the nitroprusside. Variable temperature magnetic susceptibility measurements (4.0–180.0 K) show the occurrence of very weak antiferromagnetic interactions between the copper(II) ions with $\mathbf{zJ} = -0.410 \text{ cm}^{-1}$.

Introduction
In past decades there has been much interest in the study of pentacyanonitrilotetratetraacetate hydrates of transition metal elements because of their important roles in molecular sieves, cation exchangers, electron scavengers and radionuclide sorbents [1–3]. It has been reported that the nitroprussides have also currently been used as reversible inhibitors of superoxide dismutases [4]. Recently, a few cyanide-bridged compounds based on the nitroprusside anion have been reported which exhibit weak antiferromagnetic interactions between the paramagnetic metal ions through the diamagnetic anions [Fe(CN)₅NO]²⁻ [5–7]. Our interest is mainly focused on the molecular-based magnets, including the azide-, cyanide-, oxamidato-, thiocyanato-, carboxynato-bridged, etc. complexes [8–10]. In order to understand more thoroughly the magneto-structural correlation in the nitroprusside-bridged complexes, we have prepared a new dinuclear copper(II)–iron(II) complex. In the present paper, we report the preparation, X-ray crystal structural characterization, i.r. spectrum and magnetic properties of this compound. Cryomagnetic measurements indicates that it is weakly antiferromagnetic ($\mathbf{zJ} = -0.410 \text{ cm}^{-1}$).

Experimental

Materials
All reagents were purchased from commercial sources and used as supplied. The compound [Cu(L)]Cl₂ was prepared according to the literature method [11].

Preparation of the title complex
The complex was synthesized as follows. To a solution of [Cu(L)]Cl₂ (257 mg) in H₂O (70 cm³) was added a solution of Na₂[Fe(CN)₅NO]Æ2H₂O (180 mg) in H₂O (15 cm³). After the reaction mixture was stirred continuously for a few min, the mixture was filtered. The filtrate was kept for several days at ambient temperature and the purple-needle crystals which were formed were collected by filtration, washed thoroughly with a minimum amount of MeOH (yield: 178 mg) (Found: C, 35.7; H, 5.1; N, 29.6. C₁₇H₃₀CuFeN₁₂O₅ calcd.: C, 35.8; H, 5.3; N, 29.5%).

Physical measurements
The i.r. spectrum (400–4000 cm⁻¹) was recorded in a KBr pellet using a Nicolet 170 SX spectrophotometer. Elemental analyses (C, H, N) were carried out by the Microanalytical Service, Analysis Center for Materials, Nanjing University. Magnetic susceptibility measurements were performed on a Quantum Design MPMS-7 SQUID magnetometer in the 4.0–180.0 K range at a magnetic field strength of 10 KG. The samples were pressed into pellets to avoid orientation effects of the microcrystals. Diamagnetic corrections were made using Pascal’s constants and were subtracted from the experimental susceptibility data to obtain the molar paramagnetic susceptibilities of the complex.

Single-crystal X-ray structure determination
The data were collected at 293(2) K on a CAD4 diffractometer equipped with graphite-monochromatic MoKα radiation ($\lambda = 0.71073 \text{ Å}$) $\theta$–$2\theta$ scan mode. A purple needle crystal (0.40 × 0.15 × 0.10 mm) of the

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title complex was used for the X-ray measurement. Lattice parameters were determined from a least-squares refinement of 25 reflections with \( \theta \) angles ranging between 2.46 and 12.87°. 3520 reflections were collected altogether giving 1804 independent reflections in the 2.09° \( \leq \theta \leq 23.00^\circ \) range. Intensity data were corrected for Lorenz and polarization effects and an empirical absorption correction was performed. The intensities of three standard reflections monitored every 100 reflections throughout the data collection showed no sign of crystal deterioration. The complex (formula: \( \text{C}_17\text{H}_{39}\text{CuFeN}_{12}\text{O}_{32} \)) crystallizes in the \( P2_1/n \) space group with \( a = 12.861(3), b = 14.071(3), c = 13.541(3) \) Å, \( \alpha = \gamma = 90^\circ, \beta = 93.28(3)^\circ \). \( V = 2441.6(8) \) Å\(^3\). \( Z = 4 \). The structure was solved by the direct method and refined by a full-matrix least-squares on \( F^2 \) method. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in calculated positions (\( C - H \), 0.96 Å), assigned fixed isotropic thermal parameters at 1.2 times \( C \) thermal parameters. The hydrogen atoms were placed in the structure factor calculations. In the final difference map, the residual maxima and minima were 0.868 and -0.459 Å\(^3\), respectively. The agreement indices \( R1 = \sum ||F_o|| - |F_i||/ \sum |F_o| \) and \( wR2 = \sum w(|F_o|^2 - |F_i|^2)/ \sum w|F_o|^2 \) were used to evaluate the results. \( R1 \) and \( wR2 \) \( [I > 2\sigma(I)] \) were 0.0519 and 0.1491, respectively. All calculations were carried out on a 586 PC computer by using SHELXTL-PC Package [12].

**Results and discussion**

**FT-IR spectrum**

The i.r. spectrum shows bands due to the nitroprusside fragment and the Cu(L) group. A very strong band at 1934 cm\(^{-1}\) is reasonably assigned to the NO stretching vibration, which is almost the same as those bands reported in complexes containing the nitroprusside fragment [13–15]. The strong band at 2151 cm\(^{-1}\) may be attributed to the \( v(\text{CN}) \) of the bridging cyanides and the band at 2152 cm\(^{-1}\) may be due to the terminal uncoordinated ones.

**Description of the structure**

Selected bond distances and angles are listed in Table 1. The molecular structure of the title compound is presented in Figure 1, together with an atomic labeling scheme. The unit cell is illustrated in Figure 2.

An X-ray crystallographic analysis showed that the complex is built up of dinuclear units, linked by an elongated Cu(1) \( \cdots \) N(1a) [2.877(6) Å] contact, resulting in a one-dimensional extended chain structure. As shown in Figure 2, the individual chains are further held together by hydrogen bonds [O1 \( \cdots \) O2 \((x, y, z + 1), 2.836(11) \) Å]. Thus, an extended quasi-two-dimensional structure was formed. The distances for the Cu(1) \( \cdots \) Cu(b) and the Cu(1) \( \cdots \) Cu(1a) are 9.059 and 7.966 Å, respectively (\( a: 0.5 - x, 0.5 + y, 0.5 - z; b: 0.5 - x, 2.5 + y, 0.5 - z \)).

As shown in Figure 1, the copper atom exhibits a square-pyramidal structure with four nitrogen atoms from the L ligand occupying the equatorial positions, and one nitrogen atom from the CN\(^-\) ligand in the apical positions. The equatorial atoms [N7, N8, N9, and N10] are nearly coplanar (mean deviation = 0.0039 Å), and the copper atom lies 0.0863 Å out of this plane.