



# Cyanometallate incorporated supramolecular networks based on a nitroalkyl-substituted Cu<sup>II</sup>N<sub>4</sub> precursor: Synthesis, crystal structure, thermal and electrochemical studies

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## ABSTRACT

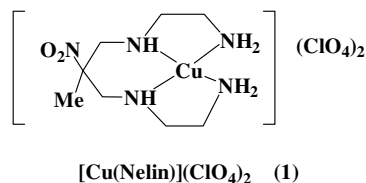
Two new copper(II) complexes, viz. [Cu(nelin)(H<sub>2</sub>O)<sub>2</sub>][Fe(CN)<sub>6</sub>] · 6H<sub>2</sub>O (**2**) and [{Cu(nelin)}<sub>2</sub>Ni(CN)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> · 2H<sub>2</sub>O (**3**), have been synthesized using [Cu(nelin)](ClO<sub>4</sub>)<sub>2</sub> (**1**) (nelin = 1,9-diamino-5-methyl-5-nitro-3,7-diazanone) as a nitroalkyl-substituted Cu<sup>II</sup>N<sub>4</sub> precursor, and their structures and supramolecular networks have been fully explored using the single crystal X-ray diffraction technique. The H-bonded 1D chains of **2** run along the *a*-axis, being generated from supramolecular synthons using cations and anions, and are further propagated into a 3D array to form irregular honeycomb-like channels which are divided into two halves, with each half accommodating a helical water chain running in opposite directions to each other. In complex **3**, the trinuclear units are arranged in successive rows in a herringbone fashion and bifurcated hydrogen bonding through the uncoordinated terminals of the [Ni(CN)<sub>4</sub>]<sup>2-</sup> units give rise to a supramolecular (4,4) network. A comparison of the PXRD pattern of complex **2** and its dehydrated form indicate marked changes in the diffraction pattern with the development of a quasi glassy nature in the dehydrated form. The electrochemical properties of **1**, **2** and **3** have been investigated in comparative ways using the cyclic voltammetric technique in aqueous and MeCN solutions with Ag/AgCl as a reference electrode. Electrochemical reduction generates the one-electron reduced nitro-radical anion. In water–alcohol glass at 77 K complex **2** exhibits a typical four-line hyperfine EPR spectra with *g*<sub>||</sub> = 2.11, *g*<sub>⊥</sub> = 2.02, *A*<sub>||</sub> = 150 Oe and *A*<sub>⊥</sub> = 5 Oe at *ν* = 9.45 MHz.

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## 1. Introduction

Crystal engineering is a rapidly expanding global discipline practiced by scientists with diverse interests in modelling, synthesis, evaluation and utilization of crystalline solids; and research on materials with desired functions and fascinating topological architectures has become an area of increasing interest in recent years [1]. A reason for this interest is the synthetic strategy used to construct these materials with a high degree of design that may lead to the development of materials with (i) tunable properties including biomimetic structures, (ii) host–guest properties similar to those observed in zeolites and (iii) interesting electronic and magnetic properties [2]. A popular approach to the design and synthesis of

such materials is to use cyanometallates [M(CN)<sub>*x*</sub>]<sup>*n-*</sup> as building blocks [3] in conjugation with discrete metal ion complexes. Architectures of 1D, 2D or 3D networks [4] can be built up by suitably tuning the various cyanometallates as well as the metal complex nodes.



Though cyanometallate bridging between copper(II) precursors of selective bi- or tri- dentate N-donor ligands is relatively common [3,5], the corresponding networks under a Cu<sup>II</sup>N<sub>4</sub> environment have been comparatively less explored [6]. The possible reasons may be due to the thermodynamic stability of the individual Cu<sup>II</sup>N<sub>4</sub> square

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planar moiety and also the reluctance to axial binding arising out of the Jahn–Teller effect.

In a continuation of our studies in this field [7], here we have strategically selected an  $N_4$ -donor copper(II) synthon, [Cu(nelin)]-( $ClO_4$ )<sub>2</sub> (**1**) (nelin = 1,9-diamino-5-methyl-5-nitro-3,7-diazanonane) with a nitroalkyl pendant attached to the main ligand frame.

The utilization of such a precursor deserves special attention since nitro compounds are used extensively as antibacterial, anti-protozoal and anticancer agents [8]. Again, such compounds in metabolic pathways undergo a one-electron reduction to generate nitro-radical anions that exhibit cytotoxicity towards cellular systems [9], causing DNA damage within the cell. Furthermore, several nitro compounds [10] and some of their metal complexes [11] are potent radio-sensitizers towards hypoxic tumour cells, and the efficiency of these drugs is related to the one-electron reduction potential of these compounds [12]. It is therefore important to study the redox behavior of these nitro compounds and the reactivity of the corresponding one-electron reduced nitro-radical anions. So far, the reactivity of these nitro-radical anions has been studied mainly by pulse radiolysis [13] and in few cases by cyclic voltammetry [14], mostly in a mixed solvent medium. The cyclic voltammetric reduction of **1** [15] and other nitro compounds [16] in protic solvents at neutral pH resulted in a single irreversible cathodic wave corresponding to the four-electron reduction of the nitro group to the hydroxylamine derivative. Recently, cyclic voltammetric reduction of a heterocyclic drug, metronidazole, in aqueous solution and aqueous DMF [17] produced the nitro-radical anion successfully. However, monitoring of the redox behavior of copper(II) complexes containing a nitro group on a ligand fragment in vivo-friendly pure aqueous medium is absolutely a new era in this dimension.

In this paper attempts have been made to highlight two relevant aspects in a justified way. First we report the syntheses, crystal structures and other physical characterizations of two new cyano complexes viz. ionic [Cu(nelin)( $H_2O$ )<sub>2</sub>]<sub>2</sub>[Fe(CN)<sub>6</sub>] · 6 $H_2O$  (**2**) and bridged {[Cu(nelin)]<sub>2</sub>Ni(CN)<sub>4</sub>}( $ClO_4$ )<sub>2</sub> · 2 $H_2O$  (**3**), by taking [Cu(nelin)]<sup>2+</sup> as the strategically starting synthon. It is noteworthy to mention here that cyanometallate incorporated copper(II) complexes in an  $N_4$ -donor diaza-diamine environment containing an –NO<sub>2</sub> pendant group has been scarcely studied [6e]. Here, the supra-molecular view not only provides an aesthetically pleasing architecture, the simultaneous transformation of **2** to a quasi-glass phase on dehydration warrants special attention in material science. In the next part, we report the detailed comparative cyclic voltammetric studies of these compounds as well as the parent complex [Cu(nelin)]( $ClO_4$ )<sub>2</sub> (**1**), especially giving emphasis on the generation of the nitro-radical anion and its effects on the subsequent redox processes in pure aqueous and in MeCN media. In this regard, it is mentionable that the nitroalkyl-substituted Cu<sup>II</sup> $N_4$  precursor and the cyanometallate incorporated complexes deserve further exploration in the context of the possibility of their potential application as radio-sensitizers in the treatment of cancer, as they are expected to serve in a better way than other organic drugs having poor solubility and high toxicity in physiological conditions compared to the macro-cyclic and acyclic complexes.

## 2. Experimental

### 2.1. Materials and methods

Materials such as aqueous formaldehyde (37%) (E-Merck, India), nitroethane (Aldrich),  $HClO_4$ , and  $K_4[Fe(CN)_6]$  (E-Merck, India) were of reagent grade and were used as received. Ethylenediamine (E-Merck, India) and triethylamine (Ranbaxy, India) were distilled over sodium metal before use. Single distilled HPLC grade MeCN (Merck Germany) was used for the electrochemical studies. All

the solutions of the complexes for the electrochemical studies were prepared freshly with double distilled water.

Elemental analyses were carried out using a Perkin–Elmer 240 elemental analyzer. Infrared spectra (400–4000  $cm^{-1}$ ) were recorded from KBr pellets on a Nicolet Magna IR 750 series-II FTIR spectrophotometer. EPR spectra of polycrystalline samples were recorded using a Varian Century Series X-band EPR spectrophotometer having 100 KHz magnetic field modulation (model E 109) and equipped with a low-temperature quartz Dewar for low-temperature measurements. Room temperature magnetic susceptibilities were recorded on a PAR vibrating sample magnetometer using  $Hg[Co(NCS)_4]$  as the calibrant. Diamagnetic corrections were estimated from Pascal's constants. TGA and DTA curves were recorded simultaneously on a Perkin–Elmer, Model Pyris Dimond TG/DTA in static dry nitrogen at a heating rate of 5 °C  $min^{-1}$ . Electrochemical measurements were carried out using a computer controlled PAR model 263A VERSASTAT electrochemical instrument with a glassy carbon disk (4 mm diameter, EG&G instrument) as the working electrode. All the results were collected at 25 ± 0.5 °C with reference to the Ag/AgCl electrode. All the solutions were purged with pure argon gas for at least 10 min prior to each experiment. Junction potentials were not corrected. Electronic spectra was recorded on an Agilent 8453 UV–Vis diode array spectrophotometer with a Peltier thermostatic temperature control facility at 25 ± 0.10 °C.

### 2.2. Syntheses

**Caution!** Since perchlorate salts are potentially explosive, only small amounts of the materials should be handled with care.

Preparation of  $Cu(ClO_4)_2 \cdot 6H_2O$ , [Cu(en)<sub>2</sub>]( $ClO_4$ )<sub>2</sub>,  $Na_2[Ni(CN)_4] \cdot 3H_2O$  and the starting material [Cu(nelin)]( $ClO_4$ )<sub>2</sub> (**1**) have been mentioned elsewhere [7,18] and the purity of each was checked by CHN analysis.

#### 2.2.1. Synthesis of [Cu(nelin)( $H_2O$ )<sub>2</sub>]<sub>2</sub>[Fe(CN)<sub>6</sub>] · 6 $H_2O$ (**2**)

To an aqueous solution of [Cu(nelin)]( $ClO_4$ )<sub>2</sub> (0.576 g, 1.0 mmol),  $K_4[Fe(CN)_6]$  (0.375 g, 1.0 mmol) dissolved in a minimum volume of water was added dropwise with constant stirring over 5 min. The precipitate that appeared initially was filtered off and the deep blue filtrate was kept in a refrigerator at 4 °C for several weeks, during which time dark brown block shaped crystals of **2** suitable for X-ray study were obtained. These were washed with cold water and dried in air at room temperature. Yield: 62% based on [Cu(nelin)]( $ClO_4$ )<sub>2</sub>. *Anal. Calc.* for  $C_{22}H_{62}Cu_2FeN_{16}O_{14}$ : C, 27.56; H, 6.47; N, 23.39. Found: C, 27.92; H, 6.88; N, 23.06%.

IR in  $cm^{-1}$  (KBr): 3582 (s,br), 3495 (w,br), 3287 (w), 3227 (w,m), 3173 (w,sh), 2959 (w), 2886 (w), 2045 (vs), 1604 (s), 1548 (s), 1346 (s).  $\mu_{eff}$  (per monomer): 1.67  $\mu_B$  at 27 °C. Electronic spectrum (water):  $\lambda_{max}$  = 532 nm ( $\epsilon$ : 61.2  $M^{-1} cm^{-1}$ ).

#### 2.2.2. Synthesis of {[Cu(nelin)]<sub>2</sub>Ni(CN)<sub>4</sub>}( $ClO_4$ )<sub>2</sub> · 2 $H_2O$ (**3**)

To an aqueous solution of [Cu(nelin)]( $ClO_4$ )<sub>2</sub> (0.576 g, 1.0 mmol),  $Na_2[Ni(CN)_4] \cdot 3H_2O$  (0.158 g, 0.6 mmol) dissolved in a minimum volume of water was added dropwise with constant stirring over 5 min. The precipitate that appeared initially was filtered off and the deep blue colored filtrate was allowed to undergo slow evaporation at ambient temperature in the open air. After several weeks, dark blue needle shape shiny crystals of **3** suitable for an X-ray study were obtained from the filtrate, which were filtered and washed with cold water followed by diethyl ether and dried in air at room temperature. Yield: 49%. based on [Cu(nelin)]( $ClO_4$ )<sub>2</sub>. *Anal. Calc.* for  $C_{20}H_{46}Cl_2Cu_2N_{14}NiO_{14}$ : C, 24.91; H, 4.77; N, 20.34. Found: C, 25.01; H, 4.41; N, 20.06%.

IR in  $cm^{-1}$  (KBr): 3609 (w), 3383 (w), 3287 (w), 3225 (w), 3151 (w), 2959 (w), 2923 (w), 2893 (w), 2141 (vs), 2124 (s), 1604 (s),

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