

Available online at www.sciencedirect.com



POLYHEDRON www.elsevier.com/locate/poly

Polyhedron 26 (2007) 1012-1022

Synthesis, crystal structure, electrochemical and kinetic studies on a cyano-bridged Cu^{II}–Ni^{II}–Cu^{II} hetero-trinuclear complex

Ambarish Ray^a, Daipayan Dutta^a, Parikshit Chandra Mondal^b, William S. Sheldrick^c, H. Mayer-Figge^c, Mahammad Ali^{a,*}

^a Department of Chemistry, Jadavpur University, Kolkata 700 032, India
 ^b Saha Institute of Nuclear Physics, Chemical Science Division, 1/AF Bidhan Nagar, Kolkata 700 064, India
 ^c Lehrstuhl fur Analytischie Chemie, Ruhr-Universitat Bochum, D-44780 Bochum, Germany

Received 17 August 2006; accepted 26 September 2006 Available online 10 October 2006

Abstract

A cyano-bridged hetero-trinuclear complex, $[Cu(HL)]_2[Ni(CN)_4]$ (2) $(H_2L = 3,9$ -dimethyl-4,8-diazaundec-3,8-diene-2,10-dionedioxime) has been synthesized and characterized by single crystal X-ray structure determination. The square planar $[Cu(HL)]^+$ cation (1), otherwise reluctant to bind axially, is converted to a square pyramidal geometry through axial ligation by the cyano group of $[Ni(CN)_4]^{2-}$ ion in di-*trans* fashion. Electrochemical studies in MeCN give (i) $E_{1/2}(Cu^{II/I}) = -0.52$ V and -0.55 V and (ii) $E_{1/2}(Cu^{III/II}) = 1.15$ and 1.23 V versus Ag/AgCl for complexes 1 and 2 respectively, whereas in aqueous solution, the corresponding $E_{1/2}(Cu^{II/I})$ appear at -0.61 V and -0.58 V. The $E_{1/2}(Cu^{III}/Cu^{II})$ appears at 1.04 V for 2 only; no such process is encountered for the complex 1 at potential ≤ 1.20 V. In addition to these there is a redox process, occurring in aqueous solution only, for the copper(II) bound ligand oxidation at 0.63 and 0.60 V versus Ag/AgCl for the complex 1 and 2 respectively. Both the complexes undergo acid catalyzed decomposition with a second-order dependence in H⁺. It is found that complex 2 decomposes at a rate ~2 times faster than the complex 1. The kinetic studies on the periodate oxidation reveal that both HIO₄ and IO₄⁻ are reacting species for the oxidation of 1, while HIO₄ is the sole reacting species for the complex 2. Again, complex 2 reacts faster than 1. An inner-sphere mechanism has been invoked for both the complexes based on large Q, the association constant values.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Cyano-bridged-hetero-trinucler complex; Crystal structure; Cyclic-voltammetry; Kinetic studies

1. Introduction

Oxime-imines represent an important class of ligands with the capability to stabilize the higher oxidation states of the central metal ion through strong ligand to metal $(L \rightarrow M) \sigma$ -donation [1]. Though several oxime-imine complexes of iron and nickel in their higher oxidation states are well reported [2], but the corresponding copper complexes are comparatively less [3].

In the late seventies, Addison et al. first selected the pseudo-macrocyclic oxime-imine ligand, H_2L ($H_2L = 3,9$ -dimethyl-4,8-diazaundec-3,8-diene-2,10-dione-dioxime) to study the *type-2* [4] copper chemistry [5]. However, they modified the original [Cu(HL)]⁺ precursor to [Cu(L)BF₂]⁺ to enhance the Lewis acidity of the copper center and monitored the axial interaction with a series of neutral or anionic monodentate ligands [5]. Since H_2L has the tendency of strong N \rightarrow M σ -donation; it reduces the Lewis acidity of the metal center in square planar [Cu(HL)]⁺ moiety making it reluctant to exhibit coordination flexibility, which is further assisted due to Jahn Teller effect.

^{*} Corresponding author. E-mail address: mali@chemistry.jdvu.ac.in (M. Ali).

^{0277-5387/\$ -} see front matter @ 2006 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2006.09.095



In our earlier report, we have been able to extend the coordination number of copper(II) under a sterically congested N_4 donor macrocyclic environment [6]. In an extension to such efforts, here, we have considered a comparatively reluctant $[Cu(HL)]^+$ chromophore to investigate its axial interaction with the tetracyanonickelate ion.

Again, the chemistry of cyano-bridged coordination complexes of transitional metal ions is of contemporary interest due to remarkable diversity in their structural topologies and indeed, it is a popular approach for designing the construction of different supramolecular architectures with unusual and interesting properties [7]. Among various cyanometalates, the tetracyanonickelate anion $[Ni(CN)_4]^{2-}$ exhibits bridging character involving either one, two, three or four of the cyano groups and all four possibilities have been found [7]. Although a few copper(II) complexes with tetracyanonickelate bridged 1D [8], 2D [9] and even 3D [9b] structures have been reported recently, the number of structural studies on discrete molecules is surprisingly low [10] and such complexes are prepared mainly by utilizing various N1, N2 or N3 donor ligands. Moreover, there is only a few reports on structural studies of such discrete tetracyanonickelate bridged copper(II) complexes under an N₄ donor ligand environment [11] and to the best of our knowledge this is the first report on an oxime-imine like N₄ donor pseudo-macrocyclic precursor.

On the other hand, from the chemical redox point of view, periodate is thought to be a typical inner-sphere oxidant often featuring diverse mechanistic behavior [12]. Though, there are reports on the oxidation of some inorganic species with a few copper(III) oxime-imine complexes [13], corresponding kinetic studies on the oxidation of copper(II) complexes by inorganic oxidant have not yet been reported. So a kinetic study on the oxidation of the cyano-bridged complex, [Cu(HL)]₂[Ni(CN)₄] · 4H₂O (2) along with the parent complex, $[Cu(HL)]ClO_4 \cdot 2H_2O$ (1) by periodate would be valuable and interesting mechanistically. In this article we report synthesis, crystal structure, electrochemical and kinetic studies on the periodate oxidation on a cyano-bridged Cu(II)-Ni(II)-Cu(II) heterotrinuclear complex 2. A parallel electrochemical and kinetic studies on the parent complex 1 reveals that there is a distinct difference in behavior of 2 over 1 due to the presence of $[Ni(CN)_4]^-$ in 2.

2. Results and discussion

2.1. Description of structure of $[Cu(HL)]_2[Ni(CN)_4] \cdot 4H_2O(2)$

Complex 2 crystallizes in the monoclinic space group C2/c and exhibits crystallographic C_2 symmetry. The asymmetric unit contains half of the formula unit along with three water molecules. The molecular structure of the complex 2 consists of a discrete hetero-trinuclear species (Cu-Ni-Cu) with the copper-copper separation of 9.778 Å by severely bent cyano bridging $[C(8)-N(5)-Cu, 143.7(4)^{\circ}]$ of $[Ni(CN)_4]^{2-}$ ion in di-*trans* fashion; along with four water molecules. The bonding arrangement of this trinuclear unit is shown in Fig. 1 and selected bond distances and angles in Table 1. Such type of cyano bridging of $[Ni(CN)_4]^{2-}$, leaves two other trans CN groups as terminal, and is comparable to $[Cu(bappz)]_2[Ni(CN)_4] \cdot (ClO_4)_2$ [11a] [bappz = 1,4bis(3-aminopropyl)piperazine]. The coordination geometry about the copper atom is best described by a square pyramid with the geometrical factor $\tau = 0.01$ [14]. The four nitrogen atoms of the H₂L ligand construct the basal plane and the nitrogen atom of the bridging cyanide occupies the apical position. The copper atom is situated 0.302 Å above the plane towards the apical direction. This makes the basal angles N(1)-Cu-N(3), 161.81(2)° and N(2)-Cu-N(4), 162.64° to deviate significantly from 180° and the four N(5)–Cu–N(x) [x = 1, 2, 3 and 4] angles are larger than 90° (avg. $98.82(2)^{0}$) indicating that the coordination geometry around each copper(II) atom is a distorted square pyramid. The average Cu-N bond length (1.964(4) Å) at the basal plane is comparable with the complex $[Cu(HL)]ClO_4$. $1/2CH_3OH[15]$. However, in that complex each copper atom of monomeric $[Cu(HL)]ClO_4 \cdot 1/2CH_3OH$ unit is further very weakly coordinated to an oxime oxygen (average Cu-O distances of 2.492 (4) Å) of the adjacent equivalent unit to form a singly bridged zigzag chain, whereas, a discrete trinuclear structure is prevailing for complex 2 with no possibility of formation of such oxime oxygen bridged Cu-O bonds.

From the charge balance considerations, it is evident that out of two *cis* oxime groups of each asymmetric unit, one is deprotonated during complex formation and makes intramolecular H-bonding with the remaining -N-OH group. The O(1)–O(2) distance (2.520 Å) is similar to the H-bonded oxygen–oxygen distance observed in other copper–oxime complexes and supports this proposition [15,16]. The Cu–N(5) apical bond length (2.155(4) Å) is comparatively longer than the Cu–N (bridging cyanide)_{basal} (2.040(7) Å) found in [Cu(Me₆Cy)][Ni(CN)₄] [6]. In contrast, Cu–N axial bond lengths for several such cyano bridged copper(II) complexes fall in the range 2.147–2.677 [11a,11b] which are comparable to the Cu–N(5) axial bond length in **2** and indicate the inclination of Cu atom towards the axial site (*vide infra*).

The C-end of the cyano ligand produces a strong field effect, while the N-end behaves as medium ligand with a ligand field lower than that of NH₃. Generally, C–N dis-



Fig. 1. ORTEP view of the trinuclear unit of **2**. Hydrogen atoms and water molecules are omitted for clarity. (Thermal ellipsoids are represented at the 30% probability level.)

Table 1 Selected bond lengths (Å) and angles (°) for complex 2

	1
Cu(1)–N(1)	1.961(4)
Cu(1)–N(2)	1.950(4)
Cu(1)–N(3)	1.972(4)
Cu(1)–N(4)	1.972(4)
Cu(1)–N(5)	2.155(4)
N(1)–O(1)	1.336(5)
N(4)–O(2)	1.339(5)
N(5)-C(8)	1.134(6)
N(6)-C(9)	1.152(7)
N(2)–Cu(1)–N(1)	80.9(2)
N(2)-Cu(1)-N(3)	98.7(2)
N(1)-Cu(1)-N(3)	161.8(2)
N(2)-Cu(1)-N(4)	162.6(2)
N(1)-Cu(1)-N(4)	95.1(2)
N(3)-Cu(1)-N(4)	79.7(2)
N(2)-Cu(1)-N(5)	97.1(2)
N(1)-Cu(1)-N(5)	95.2(2)
N(3)-Cu(1)-N(5)	102.8(2)
N(4)-Cu(1)-N(5)	100.2(2)
O(1)–N(1)–Cu(1)	122.2(3)
O(2)-N(4)-Cu(1)	123.2(3)
C(8)–N(5)–Cu(1)	143.7(4)
N(5)-C(8)-Ni(1)	178.3(5)
N(6)-C(9)-Ni(1)	177.8(5)

tances fall in the range 1.12-1.16 and no difference is found whether it is a terminal or bridging ligand [7]. In complex **2**, the C–N distances for the bridging and terminal cyanide groups are 1.134 (6) Å and 1.152(7) Å respectively and conform to the above proposition.

The Ni–C bond distances in $[Ni(CN)_4]^{2-}$ fall in the range 1.856(5)–1.859(5) Å for both bridging and terminal cyano groups and are very close to the ideal value of 1.86 [17]. The $[Ni(CN)_4]^{2-}$ moiety in **2** effectively retains its original square planar geometry and this is evidenced by the fact that all the Ni–C–N bond angles fall in the narrow range of 177.8(5)–178.3(5)°. Such rigidity of the square planer structure is generally seen for $[Ni(CN)_4]^{2-}$ in various bridging structures regardless of different modes of bridging [7].

As it is already known to us that lattice water molecules present in the crystal play a unique and ubiquitous role, not only to impart stability of the complex but simultaneously help to build up the supramolecular as well as the biological architectures. The arrangement of lattice water molecules in the present complex is highly ordered and produces a water column viewed down the b axis (Fig. 2).

2.2. IR study

The positions of the relevant IR bands were listed in the experimental section. For cyano complexes the absorption bands due to v_{CN} stretching vibrations are very characteristic. In the free tetracyanonickelate anion this absorption band appears at 2128 cm⁻¹ [17]. On bridging via N atom this band shifts to higher wave number. Here two v_{CN} IR



Fig. 2. Water column of the lattice water molecules (viewed down the b axis).

bands appeared at 2118(vs) and 2135(s) cm⁻¹ for **2** can be assigned to the terminal and bridging cyanides respectively [6]. The broad v_{O-H} band at 3389 cm⁻¹ can assure the presence of O-H···O hydrogen bonded oxime proton [16] as well as the hydrogen bonded lattice water molecules. All the other bands appear more or less at their usual positions.

2.3. Thermal analyses

Thermal decomposition of complex **2** starts at *ca*. 41 °C and consequently, the complex eliminates its uncoordinated four water molecules and the process continues up to *ca*. 58 °C (found/calcd.: 6.45/6.43% with respect to loss of wt%). This is accompanied by a small *endo*-effect on the DTA curve at *ca*. 54 °C. The anhydrous complex [Cu(HL)]₂[Ni(CN)₄] maintains its thermal stability upto *ca*. 171 °C, after which it undergoes an immediate exothermal decomposition with a DTA curve maxima at *ca*. 201 °C. The decomposition of the complex is complete at *ca*. 200 °C, giving CuO and NiO as the final products (found/calcd.: 81.65/81.64% with respect to loss of wt%).

2.4. Magnetic property

The room temperature (298 K) effective magnetic moment per monomer of complex **2** is $1.78\mu_B$ and is comparable with the spin only value $(1.73\mu_B)$ for ideally monomeric copper(II) complexes. The large Cu···Cu separation (9.778 Å) in between two monomeric units *via* diamagnetic tetracyanonickelate bridging, weakens the chance of magnetic interactions in the complex.

2.5. EPR studies

Room temperature solid state EPR of the polycrystalline sample of the complex 2 is typical for mononuclear copper(II) complexes with axial distortion and the elongation of axis is characterized by $g_{\parallel} = 2.134 \pm 0.005$ and $g_{\perp} = 2.022 \pm 0.002$. Simulation of this signal using the Lorentzian function [18] of the individual EPR line gives: $g_{\parallel} = 2.13$, $g_{\perp} = 2.02$, $A_{\parallel} = 40$ Oe, $A_{\perp} = 5$ Oe with $\Delta H = 40$ Oe at v = 9.517 GHz. The observed values $(g_{\parallel} > g_{\perp})$ confirm that the unpaired electron resides in the $d_{x^2-v^2}$ orbital.

2.6. Electrochemical studies

The electrochemical properties of the parent complex $[Cu(HL)]ClO_4 \cdot 2H_2O$ (1) and that of complex $[Cu(HL)]_2$ - $[Ni(CN)_4] \cdot 4H_2O$ (2) were investigated using the cyclic voltammetric technique in aqueous and MeCN solutions. Tetrabutyl ammonium perchlorate (TBAP, 0.1 mol L⁻¹) was used as the supporting electrolyte in MeCN solution, while 0.1 M NaClO₄ was used in aqueous solution. For comparison of the data obtained in aqueous solution, cyclic voltammetry of the free ligand (H₂L) was also carried out under similar conditions. All the electrochemical data are summarized in Table 2.

Fig. 3a shows the cyclic voltammogram for complex 2 in MeCN $(1.0 \times 10^{-3} \text{ mol } \text{L}^{-1})$ with a well defined cathodic wave for copper(II) to copper(I) reduction at a potential ca. -0.60 V, for which the reverse scan gave an anodic wave at ca. -0.50 V and the corresponding $E_{1/2}$ was estimated as -0.55 V versus Ag/AgCl. The peak potentials were invariant of scan rates and i_{pc} versus $v^{1/2}$ were linear passing through origin, where i_{pc} is the cathodic peak current and v is the scan rate in V s⁻¹. Though the ΔEp value was slightly higher than that for the Nernstian behavior it may be assumed as a reversible process with a i_{pa}/i_{pc} value approximated to unity. When the scan was continued further to more negative potential, it gave an irreversible reduction peak at potential ca. -1.75 V versus Ag/AgCl (not shown in the figure). However, this reduction process has not been investigated further. In the anodic potential region, a quasi-reversible one electron oxidation of copper(II) to copper(III) was observed with $\Delta E p = 0.16$ V and $E_{1/2} = 1.23$ V versus Ag/AgCl. It is important to note that the both anodic and cathodic peak positions were invariant with scan rates in the range of 0.05–0.8 V s⁻¹. The diffusion co-efficient [19] value of the complex 2 was determined and shown in Table 2.

Electrochemical reduction and oxidation behavior of the parent complex 1 was found behave similarly in MeCN. Fig. 3b shows a typical voltammogram for the cyclic voltammetry of the parent complex in MeCN with glassy carbon working electrode. The quasi-reversible reduction process appeared at a slightly more positive potential than that in complex 2 under the similar condition and also the voltammetric peak current was consistent with a slightly greater diffusion co-efficient as shown in Table 2. It is important to note that the intensity of the anodic peak for the oxidation of copper(I) to copper(II) in the reverse scan was greatly reduced with the formation of a desorption peak at *ca.* -0.20 V. Here also the second reduction peak, which was again irreversible, was not investigated further.

Cyclic voltammetric studies in MeCN indicate that the complex 2 is reduced at more negative potential (Fig. 3a)

101	6
-----	---

Compound	Solvent	Supporting electrolyte (0.1 M)	$Ep_{c}(V)$	$Ep_{a}(V)$	$\Delta E p$ (V)	$E_{1/2}$ (V)	$D (\rm cm^2 s^{-1})$
[CuHL]ClO ₄ · 2H ₂ O (1)]	MeCN	TBAP	1.12	1.19	0.07	1.15 ^c	8.9×10^{-5}
			-0.58	-0.47	0.11	-0.52^{d}	2.8×10^{-5}
	water	NaClO ₄	0.37	0.89	0.52	0.63 ^b	
			-0.65	-0.58	0.07	-0.61^{d}	
$[Cu(HL)]_2[Ni(CN)_4] \cdot 4H_2O$ (2)	MeCN	TBAP	1.15	1.31	0.16	1.23 ^c	3.9×10^{-5}
			-0.60	-0.50	0.10	-0.55^{d}	6.8×10^{-5}
	water	NaClO ₄	0.98	1.1	0.12	1.04 ^c	2.7×10^{-5}
			0.36	0.84	0.48	0.60^{b}	
			-0.63	-0.52	0.11	-0.58^{d}	5.3×10^{-5}
H ₂ L	water	NaClO ₄	0.49	0.73	0.24	0.61 ^b	

Table 2 Electrochemical parameters^a of the compounds

^a Maximum error \pm 7%; all potentials are measured against Ag/AgCl reference electrode.

^b $E_{1/2}$ for ligand oxidation.

^c $E_{1/2}$ for Cu^{III}/Cu^{II} couple.

^d $E_{1/2}$ for Cu^{II}/Cu^I couple. $E_{1/2}$ is determined as $1/2(Ep_c + Ep_a)$.



Fig. 3. Cyclic voltammograms of complex 1 (b) and 2 (a) in MeCN using a glassy carbon electrode and TBAP (0.10 M) as supporting electrolyte at 100 mV s⁻¹ scan rate.

in comparison to that of the parent complex and this is attributed due to the axial ligation of $[Ni(CN)_4]^{2-}$ to $[Cu(HL)]^+$ precursor through nitrogen end (*vide supra*).

In aqueous solution the cyclic voltammetry of the complex **2** (Fig. 4a and b) showed a reduction behavior very similar to that observed in MeCN with a quasi-reversible reduction of Cu^{II}/Cu^I at a $E_{1/2}$ of -0.58 V versus Ag/AgCl. But in contrast, the oxidation behavior in MeCN was completely different from that in aqueous solution. Oxidation of copper(II) takes place at a $E_{1/2}$ of 1.04 V versus Ag/AgCl which was shifted to a lower potential in comparison to that observed in MeCN. Oxidation of copper(II) or reduction of copper(III) involves a fast proton transfer which is facilitated in aqueous solution, and as a result the redox potential is shifted to a lower region. This is a kind of proton-coupled electron transfer reaction and very common



Fig. 4. Cyclic voltammograms of complex 1 (c) and 2 (a and b) in water using a glossy carbon electrode and NaClO₄ (0.10 M) as supporting electrolyte at different scan rates. Inset is the cyclic voltammogram of H_2L under the same conditions.

for many nickel(II) and iron(II) complexes of analogous ligands [2]. Further, in addition to the oxidation of copper(II) to copper(III) another anodic wave was noticed at $Ep_a = 0.84$ V having a reduction wave in the cathodic scan at *ca*. 0.36 V with $E_{1/2} = 0.60$ V *versus* Ag/AgCl and was assigned to a quasi-reversible oxidation of the copperbound ligand. It is worth-mentioning here that when the free ligand H₂L was scanned under the similar condition (Fig. 4 inset), an almost identical oxidation of the ligand at $E_{1/2} \sim 0.61$ V was observed. Thus it may be suggested that this quasi-reversible oxidation process is due to oxidation of the copper-bound ligand.

The electrochemical behavior of **1** (Fig. 4c) was also studied in aqueous solution under the similar condition.

It showed a quasi-reversible reduction of copper(II) to copper(I) with a $E_{1/2}$ at around -0.61 V versus Ag/AgCl. It also showed an oxidation process having $E_{1/2} \sim 0.63$ V which is assigned to the quasi-reversible oxidation of the metal bound ligand. It is however surprising that we could not get any wave for the oxidation of copper(II) to copper(III) in the potential range up to 1.2 V versus Ag/AgCl.

The chemical and electrochemical oxidation of the parent complex is highly pH sensitive and those were studied in detail by Sulfab et al. [3]. They claimed that the $E_{1/2}$ values for the oxidation of copper(II) to copper(III) of the parent complex are 0.955 V, 0.933 V and 0.895 V versus SCE at the pH 3.63, 4.00 and 4.59 respectively [3b]. This is in agreement with the decrease of electrode potential with increasing pH. Such consistency holds good over the pH range 1.2-5.0 [13]. However at higher pH the situation seems peculiar. Our cyclovoltammetric study of the parent complex 1 was carried out at pH 6.58 and under such condition the ligand is very likely to undergo fast internal oxidation and consequently destabilize the copper(III) complex. Such ligand oxidation may be the prime reason for the absence of finding any oxidation peak for copper(II) to copper(III) oxidation at ca 1.20 V. However, in complex 2 at pH 6.32, the presence of axial σ -donation from $[Ni(CN)_4]^{2-}$ through N atom may be responsible for stabilization of copper(III) complex under an oxidized ligand environment. Interestingly, at pH < 5.0, no ligand oxidation for both 1 and 2 was observed and this resembles the earlier trend [3b]. And finally, it is noteworthy to mention here that such ligand oxidation in the anodic part dose not arise in complex 1 as well as in 2 in MeCN, and hence the previous claim of ligand oxidation at 1.05 V versus SCE by Addison et al. in the same solvent seems surprising [5].

2.7. Kinetic study

The kinetics of oxidation of the complexes 1 and 2 by periodate, I^{VII} , was carried out in the range $[H^+] = (1.0 - 1)^{-1}$ $50.0 \times 10^{-3} \text{ mol } \text{L}^{-1}, [\text{I}^{\text{VII}}]_{\text{t}} = (0.1-10.0) \times 10^{-3} \text{ mol } \text{L}^{-1} (\text{t})$ represents total) at $\mu = 0.50 \text{ mol } \text{L}^{-1}$ (Na₂SO₄) and at temperature 25 °C. Kinetics were followed under pseudo-firstorder conditions taking complexes as the minor component $(2 \times 10^{-4} \text{ mol } \text{L}^{-1})$ and by monitoring the increase in absorbance due to the formation of copper(III) complexes at the wavelengths of maximum absorption (515 nm). Fig. 5 represents the time-resolved spectra generated from a kinetic trace. The reactions were clean for more than four half lives, after which kinetic traces become irregular, maybe due to decomposition or for some other reactions. As we are interested to note the chemical redox behavior of these complexes towards periodate as an oxidant, we looked into the initial oxidation process. Pseudo-first-order rate constants (k_{obs}/s^{-1}) were obtained by fitting the kinetic curves with the help of a suitable single exponential computer-fit program and the results obtained in more than two determinations fall in the error limit \pm 5%.



Fig. 5. Spectral scan showing the conversion of copper(II) to copper(III) of the complex **2** under kinetic conditions. First spectrum was for the complex and second was taken immediately after mixing with $[I^{VII}] = 0.0007$ M at $[H^+] = 0.01$ M. Successive spectra were taken in an arbitrary time scale.

2.7.1. Acid catalyzed decomposition of parent complex (1) and complex (2)

It was observed that both the complexes 1 and 2 undergo acid catalyzed decomposition. So an attempt was taken to study the kinetics of acid catalyzed decomposition these complexes. For this purpose, $[H^+]$ variation experiments were conducted in the range 0.01-0.20 mol L⁻¹ at $\mu = 0.50$ mol L⁻¹ (Na₂SO₄) and 25 °C, where single exponential decay curves manifests a firstorder dependence on the complex. It is interesting to note that this decomposition rate constant (k_{obs}/s^{-1}) is secondorder in H⁺ and can best be described as the rapid protonation of oximato-oxygen and then second protonation on one of the two imine nitrogen followed by decomposition of the protonated species in a rate determining step and has been described in Eq. (1). Corresponding data have been listed in Table 3. Such protonation weaken both the Cu-N(R)(OH) and $Cu-N(R^{1})(R^{2})$ bonds and causes the decomposition of the complexes.



Plots of k_{obs} versus [H⁺] give non-linear curves (Fig. 6) with increasing slope which were solved by using suitable com-

Table 3 Summary of pseudo-first-order rate constants for the acid catalyzed decomposition of complexes 1 and 2 at $\mu = 0.50 \text{ mol } \text{L}^{-1}$ (Na₂SO₄) and 25 °C

[H ⁺]/M	$10^4 \times k_{\rm obs} \ (1)/{\rm s}^{-1}$	$10^4 \times k_{\rm obs} \ (2)/{\rm s}^{-1}$		
0.01	1.46	3.60		
0.05	3. 12	9.01		
0.10	9.10	21.6		
0.15	25.7	52.1		
0.20	41.6	90.0		

puter-fit program to Eq. (1a) to get $k^{\rm H} = 0.098 \pm 0.03 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ and $n = 1.95 \pm 0.17$ for **1** and $k^{\rm H} = 0.20 \pm 0.05 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ and $n = 1.93 \pm 0.13$ for **2**

$$k_{\rm obs} = k^{\rm H} [{\rm H}^+]^n \tag{1a}$$

The acid catalyzed decomposition rate constant, $k^{\rm H}$, for **2** is found to be ~2 times higher than that of complex **1** and can be attributed to the axial coordination of $[\rm Ni(CN)_4]^{2-}$ to the copper(II) center which probably destabilizes the system and facilitates this process.

2.7.2. Oxidation of 1

The dependence of rate on $[I^{VII}]_t$ was carried out at $[H^+] = 0.01 \text{ mol } L^{-1}$ and a plot of k_{obs} versus $[I^{VII}]_t$ shows an initial rapid increase in rate with $[I^{VII}]_t$ followed by slower increase and then becomes almost independent on $[I^{VII}]_t$ (Fig. 7). Such a dependence of rate is best described by Eq. (2). The factor 2 comes from the stoichiometry of the reactions

$$k_{\rm obs} = 2 \frac{kQ[\mathbf{I}^{\rm VII}]}{1 + Q[\mathbf{I}^{\rm VII}]} \tag{2}$$

A non-linear least-square computer-fit program provides $k = (1.37 \pm 0.06) \times 10^{-2} \text{ s}^{-1}$ and $Q = (1002 \pm 166) \text{ L mol}^{-1}$. The dependence of k_{obs} on [H⁺] in the range 0.001–0.01 mol L⁻¹ at [I^{VII}]_t = 0.0007 mol L⁻¹, where a strict first-order dependence on [I^{VII}]_t holds, is shown in



Fig. 6. Plot of pseudo-first-order rate constants (k_{obs}/s^{-1}) vs. [H⁺] for the acid catalyzed decomposition of complexes 1 and 2 at $\mu = 0.50$ M (Na₂SO₄) and 25 °C.



Fig. 7. Plots of k_{obs} vs. [I^{VII}] for the oxidation of complexes 1 and 2 at [H⁺] = 0.01 M.

Fig. 8. The presence of measurable intercept on the rate axis indicates that both protonated (HIO₄) and deprotonated (IO_4^-) species are reactive towards **1**. The following reaction sequence could be framed to explain the above observation:

$$[\operatorname{Cu}(\operatorname{HL})]^{+} + \operatorname{HIO}_{4} \stackrel{\mathcal{O}_{1}}{\rightleftharpoons} \{[\operatorname{Cu}(\operatorname{HL})]^{+}, \operatorname{HIO}_{4}\}$$
$$\stackrel{k_{1}}{\rightarrow} [\operatorname{Cu}(\operatorname{L})]^{+} + 2\operatorname{H}^{+} + \operatorname{IO}_{4}^{-}$$
(3)

$$[\operatorname{Cu}(\operatorname{HL})]^{+} + \operatorname{IO}_{4}^{-} \stackrel{Q_{2}}{\rightleftharpoons} \{[\operatorname{Cu}(\operatorname{HL})]^{+}, \operatorname{IO}_{4}^{-}\}$$
$$\stackrel{k_{2}}{\rightarrow} [\operatorname{Cu}(\operatorname{L})]^{+} + \operatorname{H}^{+} + \operatorname{IO}_{4}^{\cdot-}$$
(4)

The radical thus generated reacts in a fast step with another copper(II) complex to give $[Cu(L)]^+$ and IO_3^- as the final products (Eq. (5)) to account for an overall 2:1 stoichiometry of the reaction with respect to the complex, which is common to the most of reactions involving periodate as oxidant in acid medium [12]. The fast decomposition of the copper(III) complex generated thereby precludes the



Fig. 8. Plots of k_{obs} vs. [H⁺] for the oxidation of complexes 1 and 2 at [I^{VII}] = 0.0007 M.

determination of the stoichiometry of the reaction under the kinetic conditions

$$[Cu(HL)]^{+} + IO_{4}^{-} + H^{+} \stackrel{\text{fast}}{\to} [Cu(L)]^{+} + IO_{3}^{-} + H_{2}O \qquad (5)$$

The rate law derived is shown in Eq. (6)

$$k_{\rm obs} = 2 \frac{k_1 Q_1 [{\rm H}^+] + k_2 Q_2 K_a}{\{K_a + [{\rm H}^+]\}} [{\rm I}^{\rm VII}]_t$$
(6)

As, HIO₄ is a strong acid, it is imperative that K_a (0.023) [20] > [H⁺] and Eq. (6) where, $k = k_{obs}/2[I^{VII}]_t$, turns to Eq. (7) and easily explains the observed dependence of rate on [H⁺],

$$k = (k_1 Q_1 / K_a) [\mathrm{H}^+] + k_2 Q_2 \tag{7}$$

The linear fit of data to [H⁺] gives parameters as: $k_1Q_1/K_a = (6.75 \pm 0.54) \times 10^2 \text{ s}^{-1}$, $k_1Q_1 = 15.5 \text{ L mol}^{-1} \text{ s}^{-1}$ and $k_2Q_2 = (6.00 \times 0.33) \text{ L mol}^{-1} \text{ s}^{-1}$.

2.7.3. Oxidation of 2

The dependence of rate on $[I^{VII}]_t$ was carried out at $[H^+] = 0.01$ M and a plot of k_{obs} versus $[I^{VII}]_t$ shows an initial rapid increase in rate with $[I^{VII}]_t$ followed by slower increase and then becomes almost independent on $[I^{VII}]_{t}$ (Fig. 7) and best represented by rate law (2). The effect of [H⁺] on the oxidation rate was investigated in the range $[H^+] = 0.001 - 0.05 \text{ mol } L^{-1}$ at $[I^{VII}]_t = 0.0007 \text{ mol } L^{-1}$, where a strict first-order dependence on it holds good. The rate increases initially rapidly with increasing $[H^+]$, then slowly and finally becomes almost independent of [H⁺] resulting in a plateau with a negligibly small or no intercept on the rate axis (Fig. 8). Such a dependence of rate on [H⁺] indicates that anionic forms of periodic acid $(H_4IO_6^{-} \text{ or } IO_4^{-})$ are un-reactive towards the complex leaving H_5IO_6 or $HIO_4 \cdot 2H_2O(H_2A)$ as the sole oxidant. The proton association of periodate anion, which can exist as $H_4IO_6^-$ and IO_4^- and $[HA^-]_t = [IO_4^-] + [H_4IO_6^-]$, can be described by Eq. (8) [12d]

$$\mathbf{H}\mathbf{A}^{-} + \mathbf{H}^{+} \stackrel{\kappa}{\rightleftharpoons} \mathbf{H}_{2}\mathbf{A} \tag{8}$$

thus, *K* actually represents the apparent proton association constant reported to have value in the range 43–61 L mol⁻¹ at 25 °C [12d,21]. Considering the foregoing discussion, a reasonable reaction sequence may be proposed to account for the oxidation of $[Cu(HL)]_2[Ni(CN)_4]$ by periodic acid

$$[\operatorname{Cu}(\operatorname{HL})]^* + \operatorname{H}_5\operatorname{IO}_6 \stackrel{\mathcal{Q}}{\rightleftharpoons} \{[\operatorname{Cu}(\operatorname{HL})]^*, \operatorname{H}_5\operatorname{IO}_6\}$$
(9)

$$\{[Cu(HL)]^*, H_5IO_6\} \xrightarrow{k} [Cu(L)]^+ + H_3IO_5 \xrightarrow{\cdot} + H_3O^+$$
 (10)

Here $[Cu(HL)]^*$ represents the modified species of $[Cu(HL)]_2[Ni(CN)_4]$ where $[Ni(CN)_4]^{2-}$ may be weakly coordinated to a copper center in solution. The radical thus generated reacts with another molecule of the complex in a rapid step to yield $H_3IO_5^{2-}$ as the final reduction product of periodate, which is common to the most of reactions involving periodate as oxidant in acid medium and corresponds to a 2:1 stoichiometric reactions [12]. Here also

the fast decomposition of the copper(III) complex precludes the determination of the stoichiometry of the reaction under the kinetic conditions

$$-d[C]/dt = 2\frac{kQ[H_5IO_6]}{1+Q[H_5IO_6]}[C]$$
(11)

Here, $C = [Cu(HL)]_2[Ni(CN)_4]$. While expressing H₅IO₆ in terms of total periodate concentration Eq. (11) turns to Eq. (12).

$$k_{\rm obs} = 2 \frac{kQK[{\rm H}^+][{\rm I}^{\rm VII}]_{\rm t}}{1 + \{K[{\rm H}^+](1 + Q[{\rm I}^{\rm VII}]_{\rm t})\}}$$
(12)

Eq. (12) was solved for k and K by fitting k_{obs} as a function of $[I^{VII}]_t$ keeping Q fixed at 100, and the evaluated parameters are: $k = (1.97 \pm 0.03) \times 10^{-2} \text{ s}^{-1}$ and $Q = 3263 \pm 0.03$ 170 L mol⁻¹. Again fitting k_{obs} as a function of [H⁺] with Q = 3263 as a fixed parameter gives parameters: $\bar{k} = (2.21 \pm 0.05) \times 10^{-2} \text{ s}^{-1}$ and $K = (85 \pm 7) \text{ L mol}^{-1}$. It is to be mentioned here that very good fitting of two separate sets of data for $[H^+]$ and $[I^{VII}]_t$ indicates the self-consistency of the proposed mechanism. The evaluated proton association equilibrium constant (K = 85) for H₄IO₆⁻ is in reasonable agreement with the literature value of K = 61[12d]. The very large association constant also consistent with an inner-sphere mechanism which may occur either through hydrogen bonding between the hydrogen atom on H_5IO_6 and O^- of the oxime-imine ligand or the oxygen atom of H₅IO₆ and the undissociated H on the oxime-imine ligand. Another possibility is that H₅IO₆ may directly coordinate to the metal center. The main objection of this proposition is the absence of the reactivity of IO_4^- or $H_4IO_6^-$, which may be a better coordinating ligand than H_5IO_6 .

It is to be mentioned here that the acidity of reaction media were so chosen for both the reactions that the acid catalyzed decomposition of the complexes is negligible compare to the electron transfer process. The complex [Cu(HL)]₂[Ni(CN)₄] may undergo dissociation to give individual ions $[Cu(HL)]^+$ and $[Ni(CN)_4]^{2-}$; $[Cu(HL)]_2$ [-Ni(CN)₄] should then behave identically to that of parent compound prepared separately. As the dependences of rate (k_{obs}/s^{-1}) on $[I^{VII}]_t$ and $[H^+]$ for the reaction with $[Cu(HL)]_2[Ni(CN)_4]-I^{VII}$ differ from that of $[Cu(HL)]^+-I^{VII}$ reaction, this may arise due to the presence of $[Ni(CN)_4]^{2-1}$ ions in the former which may form an ion pair with $[Cu(HL)]^+$ or may be coordinated to the metal center causing this difference. To establish this proposition we checked the dependence of k_{obs} on $[H^+]$ in presence of $[Ni(CN)_4]^{2-1}$ in the mole ratio $1:2 = [Ni(CN)_4]^2 : [Cu(HL)]^+$ and it was observed that this dependence was almost identical to that observed for $[Cu(HL)]_2[Ni(CN)_4]$ -I^{VII} reaction and support our proposition. As the acid catalyzed decomposition of complex 2 is ~ 2 times higher than complex 1, it manifests the coordination of $[Ni(CN)_4]^{2-}$ moiety to the copper center destabilizes the system. It indirectly supports the coordination of $[Ni(CN)_4]^{2-}$ moiety to the copper center over the formation of ion pair which rather will stabilize the system.

It is generally accepted that periodate reacts via innersphere mechanism and supported by its failure to oxidize $[Fe(Phen)_3]^{2+}$ (phen = phenanthroline), which requires an inner-sphere route [12c]. The oxidation of $[Cr(H_2O)_6]^{3+}$, an inert complex, was proposed to proceed by inner-sphere route assuming $[Cr(H_2O)_5(OH)]^{2+}$ as the reacting species, where the ligated OH⁻ increases the lability of the metal center [12c]. The substantially high formation constant $(Q = 3263 \pm 170 \text{ L mol}^{-1})$ suggests that the reaction proceeds through the pre-equilibrium formation of a precursor complex, an inner-sphere adduct, followed by electron transfer. Similar proposition was also advocated in the oxidation of dodecatungstocobaltate(II), a robust outersphere reactant, by periodate, where also HIO₄ was the sole reacting species [12d].

3. Conclusion

- A cyano-bridged hetero-trinuclear complex, [Cu(HL)]₂[Ni(CN)₄] · 4H₂O (2) has been synthesized and characterized by single crystal X-ray structure determination. The square planar [Cu(HL)]⁺ cation, assumes a square pyramidal geometry through axial ligation by a cyano group of [Ni(CN)₄]²⁻ ion.
- (2) The arrangement of lattice water molecules in $[Cu(HL)]_2[Ni(CN)_4] \cdot 4H_2O$ is highly ordered producing water columns viewed down the *b* axis.
- (3) Both the complexes 1 and 2 electrochemically behaves very similarly in MeCN as well as in water showing well defined quasi-reversible redox couples for Cu^{II/I} and Cu^{III/II} conversions, with the exception that the latter conversion does not arise in 1 in aqueous medium.
- (4) The copper(II) bound ligand oxidation occurs at $E_{1/2} = 0.63$ and 0.60 V versus Ag/AgCl for the complexes 1 and 2 respectively only in aqueous solution. The absence of such process in MeCN may be attributed to the fact that it is a proton-coupled electron transfer process, which is only feasible in aqueous medium. Assignment of such a process to the coordinated ligand oxidation was confirmed by carrying out parallel study with the free ligand which showed similar redox process with $E_{1/2} = 0.61$ V versus Ag/AgCl.
- (5) Both the complexes 1 and 2 undergo H^+ catalyzed decomposition with a rate second-order in H^+ and can best be described as the rapid protonation of oximato-oxygen and then second protonation on one of the two imine nitrogen followed by decomposition of the protonated species in a rate determining step. Such protonations weaken both the Cu–N(R)(OH) and Cu–N(R¹)(R²) bonds and causes the decomposition of the complexes.
- (6) Periodate oxidation of 1 and 2 reveals that both HIO_4 and IO_4^- are the reacting species for 1 while HIO_4 is the sole reacting species for 2.

(7) The slightly higher reactivity of **2** over **1** may arise due to the destabilization of complex **2** through axial ligation by $[Ni(CN)_4]^{2-}$. This is in line with the electrochemical behavior in aqueous solution.

4. Experimental

4.1. Materials and methods

All the starting materials like $Cu(CH_3COO)_2 \cdot H_2O$, CuCO₃, KOH, KCl, CH₃COONa, NaClO₄, HClO₄, HCl, H₂SO₄, MeOH, diisopropyl ether, *N*,*N*-dimethylformamide, standard buffer solutions (ACROS ORGANICS, USA) of pH 4.0 and 7.0 *etc.* were of reagent grade and used as received. 1,3-Propanediamine (E-Merck, India) was distilled by refluxing over Na metal for about an hour before use. Analytical grade diacetyl monooxime (Merck Germany), KIO₄ (Aldrich) and Na₂SO₄ (Merck Germany) were used after recrystallization. All the experimental solutions of the complexes for electrochemical and kinetic studies were prepared freshly by doubly 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 (model E 109) with 100 kHz magnetic field modulation. Room temperature magnetic susceptibilities were recorded a PAR vibrating sample magnetometer using on $Hg[Co(NCS)_4]$ as the calibrant. Diamagnetic corrections were estimated from Pascal's constants. TGA and DTA curves were recorded simultaneously on a Perkin-Elmer, Model PyrisDimond TG/DTA in static dry nitrogen at the heating rate of $5 \,^{\circ}\text{C} \,^{\text{min}^{-1}}$. 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) 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 ten minutes prior to each experiment. Junction potentials are not corrected. Electronic spectra and kinetic experiments were recorded on an Agilent 8453 UV-Vis diode array spectrophotometer with Peltier thermostatic temperature control facility at 25 \pm 0.10 °C. The pH (±0.01) measurements were carried out with a Systronics (model 335, India) digital pH-meter at 25 °C.

4.2. Syntheses

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

 $Cu(ClO_4)_2 \cdot 6H_2O$ was prepared from $CuCO_3$ and 50% $HClO_4$ by the standard method. $Na_2[Ni(CN)_4] \cdot 3H_2O$ was prepared according to standard literature procedure

[22] taking NaCN instead of KCN, and further characterized by CHN analysis. The ligand H₂L [23] and the parent complex [Cu(HL)]ClO₄ \cdot 2H₂O [5] (1) were prepared by using the literature methods and the purity was also checked by CHN analysis.

4.2.1. $[Cu(HL)]_2[Ni(CN)_4] \cdot 4H_2O(2)$

To a methanolic solution of $[Cu(HL)]^+$ (1.0 mmol, in 40 mL MeOH, generated *in situ* by mixing equimolar quantities of Cu(ClO₄)₂ · 6H₂O and H₂L) Na₂[Ni(CN)₄] · 3H₂O (0.158 g, 0.6 mmol) dissolved in a minimum volume of water, was added drop-wise with constant stirring for 5 min. The precipitate that appeared initially was filtered off and the dark brown filtrate was allowed to undergo slow evaporation at ambient temperature whereupon shiny dark brown crystals suitable for X-ray study were obtained after two weeks. Yield: 52% based on Cu. *Anal.* Calc. for C₂₆H₄₆N₁₂ O₈Cu₂Ni: C, 37.16; H, 5.52; N, 20.00. Found: C, 37.26; H, 5.51; N, 19.79%.

Selected IR in cm⁻¹ (KBr): 3389 (br), 2930 (w), 2135 (s), 2118 (vs), 1630 (m), 1541 (br, m), 1500 (w), 1431 (m), 1379 (m), 1358 (m), 1323 (m),1275 (m),1225 (m), 1115 (br), 1089 (w), 1014 (w), 692 (w), 627 (w). $\mu_{\rm eff}$ (per monomer): $1.78\mu_{\rm B}$ at 25 °C.

4.3. Crystal data collection and refinement

Intensity data for **2** was collected at 293(2) K on a Siemens P4 defractometer using graphite monochromatized Mo K α radiation ($\lambda = 0.71073$ Å.) and the ω -2 θ scan mode in the range 2.06 $\leq \theta \leq 27.51^{\circ}$. The intensities were corrected for Lorentz-polarization effects and for absorption using ψ -scans. The minimum and maximum transmission factors were 0.154 and 0.235. The structure was solved by direct methods and all non-hydrogen atoms refined anisotropically by full matrix least squares on F^2 using the SHELXTL PLUS-PC version [24] and hydrogen atoms were

Table 4

Empirical formula	$C_{26}H_{46}Cu_2N_{12}NiO_8$
fw	840.25
Crystal system	monoclinic
Space group	C2/c
a (Å)	13.263(3)
b (Å)	21.255(4)
<i>c</i> (Å)	14.131(3)
β (°)	109.44(3)
$V(A^3)$	3756.6(13)
Z	4
$T(\mathbf{K})$	293(2)
λ (Å)	0.71073
$d_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.486
$\mu (\mathrm{mm}^{-1})$	1.677
F_{000}	1704
Reflections collected/unique $[R_{int}]$	4458/4282 [0.0370]
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0583, wR_2 = 0.1408$
<i>R</i> indices [all data]	$R_1 = 0.0937, wR_2 = 0.1611$
Goodness-of-fit	1.014

included geometrically and refined isotropically except the oxime proton and those of water hydrogens of which the former is randomly disordered over its two possible ligand sites in the unit cell. Other additional information concerning the data collection and refinement of the structure is compiled in Table 4.

Acknowledgements

Financial support from the Council for Scientific and Industrial Research (CSIR), and University Grant Commission (UGC), New Delhi, India are acknowledged.

Appendix A. Supplementary material

CCDC 278585 contains the supplementary crystallographic data for the structure reported in the paper. These data can be obtained free of charge via http://www.ccdc. cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.poly.2006.09.095.

References

- (a) A. Chakravorty, Coord. Chem. Rev. 13 (1974) 1;
 (b) V.Y. Kukushkin, D. Tudela, A.J.L. Pombeiro, Coord. Chem. Rev. 156 (1996) 333;
 (c) V.Y. Kukushkin, A.J.L. Pombeiro, Coord. Chem. Rev. 181 (1999) 147;
 - (d) P. Chaudhuri, Coord. Chem. Rev. 243 (2003) 143;

(e) J.A. McCleverty, T.J. Meyer, Comprehensive Coordination Chemistry II: Ligands, vol. 1, Elsevier Science, Oxford, UK, 2004, Section 1.

[2] (a) J.G. Mohanty, R.P. Singh, A. Chakravorty, Inorg. Chem. 14 (1975) 2178;

(b) A.N. Singh, R.P. Singh, J.G. Mohanty, A. Chakravorty, Inorg. Chem. 16 (1977) 2597;

(c) A.N. Singh, A. Chakravorty, Inorg. Chem. 19 (1980) 969;

(d) K. Nag, A. Chakravorty, Coord. Chem. Rev. 33 (1980) 87;

(e) A. Chakravorty, Isr. J. Chem. 25 (1985) 99;

(f) R.A. Marusak, C. Sharp, A.G. Lappin, Inorg. Chem. 29 (1990) 2298.

[3] (a) Y. Sulfab, M.A. Hussein, N.I. Al-Shatti, Inorg. Chim. Acta 67 (1982) L33;

(b) Y. Sulfab, N.I. Al-Shatti, Inorg. Chim. Acta 87 (1984) L23.

- [4] W. Kaim, B. Schwederski, Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life, John Wiley & Sons, Inc., New York, 2001, Chapter 10.
- [5] A.W. Addison, M. Carpenter, L.K.-M. Lau, M. Wicholas, Inorg. Chem. 17 (1978) 1545.
- [6] M. Ali, A. Ray, W.S. Sheldrick, H. Mayer-Figge, S. Gao, A.I. Shames, New J. Chem. 28 (2004) 412.
- [7] J. Černák, M. Orendáč, I. Potočňák, J. Chomič, A. Orendáčová, J. Skoršepa, A. Feher, Coord. Chem. Rev. 224 (2002) 51.
- [8] (a) Z. Smékal, I. Císařová, J. Mroziński, Polyhedron 20 (2001) 3301;
 (b) P.S. Mukherjee, T.K. Maji, T. Mallah, E. Zangrando, E.L. Randaccio, N.R. Chaudhuri, Inorg. Chim. Acta 315 (2001) 249;
 (c) T.K. Maji, P.S. Mukherjee, G. Mostafa, E. Zangrando, N.R. Chaudhuri, Chem. Commun. (2001) 1368.

- [9] (a) T. Miyoshi, T. Iwamoto, Y. Sasaki, Inorg. Chim. Acta 7 (1973) 97;
 (b) J. Černák, J. Lipkowski, Monatsh. Chem. 130 (1999) 1195.
- [10] (a) H. Kurihara, S. Nishikiori, T. Iwamoto, Acta Crystallogr., Sect. C 53 (1997) 1409;
 - (b) J. Černák, J. Lipkowski, I. Potočňák, A. Hudák, Monatsh. Chem. 132 (2001) 193;

(c) J. Černák, J. Chomič, M. Dunaj-jurčo, Chem. Pap. 44 (1990) 13;
(d) C. Janiak, H.P. Wu, P. Klüfers, P. Mayer, Acta Crystallogr., Sect. C 55 (1999) 966.

[11] (a) Z. Smékal, Z. Trávníček, J. Mroziński, J. Marek, Inorg. Chem. Commun. 6 (2003) 1395;

(b) N.F. Curtis, H. Puschmann, Acta Crystallogr., Sect. C 60 (2004) 410.

- [12] (a) Y. Sulfab, A.I. Abu-Shady, Inorg. Chim. Acta 21 (1977) 115;
 (b) A.Y. Kasim, Y. Sulfab, Inorg. Chim. Acta 22 (1977) 16;
 (c) A.Y. Kasim, Y. Sulfab, Inorg. Chem. 20 (1981) 506;
 (d) M. Ali, S.K. Saha, P. Banerjee, J. Chem. Soc., Dalton Trans. (1991) 2305.
- [13] A. Hussein, Y. Sulfab, M. Nasreldin, Inorg. Chem. 28 (1989) 157, and the references therein.
- [14] (a) G.A. Mclachlan, G.D. Fallon, R.L. Martin, L. Spiccia, Inorg. Chem. 34 (1995) 254;

(b) A.W. Addison, T.N. Rao, J. Reedijk, R. Van, J. Rijn, G.C. Verschoor, J. Chem. Soc. Dalton Trans. (1984) 1349.

- [15] J.A. Bertrand, J.H. Smith, D.G. vanDerveer, Inorg. Chem. 6 (1977) 1484.
- [16] O.M. Kanderal, H. Kozlowski, A. Dobosz, J.S. Kozlowska, F. Meyer, I.O. Fritsky, J. Chem. Soc., Dalton Trans. (2005) 1428.
- [17] A.G. Sharpe, The Chemistry of the cyano complexes of the Transition Metals, Academic Press, London, 1976.
- [18] T. Vanngard, R. Aasa, W. Low (Eds.), Paramagnetic Resonance, vol. II, Academic Press, 1963, p. 509.
- [19] A.G. Bard, L.R. Faulkner, Electrochemical Methods Fundamental and Application, John Wiley & Sons, New York, 1980, p. 218.
- [20] L.G. Sillen, A.E. Martell, Stability Constants of Metal-Ion Complexes Spl. Publications no. 25, The Chemical Society, 1964, Section I, p. 226.
- [21] C.E. Crouthamel, A.M. Hayes, D.S. Martin, J. Am. Chem. Soc. 73 (1951) 82.
- [22] C. Fernelius, J. Burbage, W.C. Fernelius (Eds.), Inorganic Syntheses, vol. II, McGraw-Hill Inc., 1946, p. 227, Chapter 8.
- [23] E. Uhling, M. Friedrich, Z. Anorg. Allg. Chem. 343 (1966) 299.
- [24] G.M. Sheldrick, SHELXL '97, Program for Crystal Structure Refinement, University of Gottingen, Germany, 1997.