Inorganica Chimica Acta, *165* (1989) 83–85

A New Cyano-bridged Binuclear Complex of Pyridine-2-aldoxime with Pentacyanoferrate(II) Ions

NICOLETTA BURGER*, VLADIMIRA HANKONYI and ZLATA SMERIĆ

Department of Chemistry and Biochemistry, Faculty of Medicine, University of Zagreb, 41000 Zagreb, Šalata 3 (Yugoslavia)

(Received April 17, 1989)

Abstract

A new cyano-bridged binuclear complex of the formula $Na_5[(CN)_5Fe\text{-}NC\text{-}Fe(CN)_3(pyCHNOH)]\cdot 8H_2O$ was prepared through the interaction of sodium amminepentacyanoferrate(II) and pyridine-2-aldoxime. The complex was characterized on the basis of analytical, infrared and electronic spectral data. Mercury(II) ions catalyse the formation of the complex which indicates that pyridine-2-aldoxime behaves as a bidentate ligand.

Introduction

Although poor σ donors, mostly through the nitrogen atom, oximes are well known for their coordinating abilities and for their complexes with transition metals [1]. Like a large variety of other nitrogen containing ligands (amines, nitrogen heterocycles), many oximes are also known to bind to the $Fe(CN)_5^{3-}$ moiety producing oximatopentacyanoferrate(II) complexes [2–5]. The complexes are formed in the reactions of oximes with aquopentacyanoferrate(II) ions which have been rapidly formed from amminepentacyanoferrate(II) ions (AmP) in aqueous solutions and nitrosylpentacyanoferrate(II) ions (NP) in alkaline aqueous solutions.

Recently, a study of the (pyridine-2-carbaldoxime)-tetracyanoferrate(II) complex was published [6]. The complex was prepared according to the methods used for (1,2-diamine)tetracyanoferrate(II) chelates [7] by mixing methanol solutions of oxime and $Fe(ClO_4)_2$, followed by the addition of an aqueous sodium cyanide solution.

In the present paper, a complex is reported which is formed by the reaction of the same oxime, namely pyridine-2-aldoxime (PA-2), with aquopentacyanoferrate(II) ions, but of a different composition. It is a cyano-bridged binuclear complex, sodium pentacyanoferrate(II)-μ-cyano-tricyanooximatoferrate(II) of the formula $Na_5[(CN)_5Fe\text{-}NC\text{-}Fe(CN)_3(pyCHNOH)]\cdot 8H_2O$. The formation of this complex is catalysed by mercury(II) ions.

Experimental

All reagents used were of analytical reagent grade. Redistilled water was used throughout the experiments. Britton and Robinson buffers were prepared by mixing 100 ml of phosphoric, boric and acetic acid mixture (all 0.04 M) with different volumes of 0.20 M sodium hydroxide. Aqueous solutions of $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ (AmP) (Touzart-Matignon) were prepared 10–15 min before being used. Pyridine-2-aldoxime (PA-2) is a 'Fluka' reagent. It was recrystallized from water, melting point (m.p.) 112–113 °C. The constant ionic strength of 0.05 M was obtained by the addition of sodium chloride. The solution of mercury(II) ions was prepared by dissolving $HgCl_2$ in water.

Spectroscopic measurements of aqueous solutions were made by a UNICAM SP 600 UV spectrophotometer. IR spectra were recorded in KBr pellets.

The complex was prepared by adding the solution of 0.1220 g PA-2 (1 mmol) in 2 ml of conc. ethanol to a solution which contained 0.0326 g AmP (0.1 mmol) in 3 ml of water. Immediately after mixing, 40 μg of Hg^{2+} ions were added to the mixture and the pH of the solution was adjusted to 6 by the addition of HCl. The mixture was left in the dark. After about 2 h it was evaporated to dryness *in vacuo* and the obtained product was washed with 30 ml of ether. The yield was 0.0264 g of pure product. It was stored in a vacuum desiccator over P_2O_5. The gathered orange powder is easily soluble in water, and less soluble in ethanol. Its water solution shows a band at $\lambda = 470$–480 nm. After addition of diluted H_2O_2 the colour of the solution rapidly fades.

Flame photometry has given evidence that the complex contains 16.16% of sodium. *Anal.* Found: C, 25.06; H, 2.87; N, 21.69. Calc. for $Na_5[(CN)_5Fe\text{-}NC\text{-}Fe(CN)_3(pyCHNOH)]\cdot 8H_2O$: C, 24.78; H, 3.05; N, 21.19; Na, 15.81%.

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*Author to whom correspondence should be addressed.

0020-1693/89/$3.50

Results and Discussion

Pyridine-2-aldoxime reacts with sodium ammine-pentacyanoferrate(II) in slightly acidic, neutral and slightly alkaline aqueous media by producing an orange complex whose AmP to PA-2 ratio determined spectrophotometrically was found to be 2 to 1 [8].

The UV spectrum of the complex shows two strong absorption bands at 240 and 275 nm. The positions of these bands are identical to those of the free ligand and are assigned to π–π^* transitions within the heterocycle [9]. The other two weaker bands at 340 and 396 nm are characteristic of the complex and are very similar to those of the corresponding mononuclear constituent groups. Consequently they can be interpreted in terms of the two different chromophores in the dimer, i.e. $Fe(CN)_5$-(NC) and $Fe(CN)_4(pyCHNOH)$, and are assigned to charge-transfer transitions from the metals d(π) orbitals to the acceptor p(π^*) nitrogen orbitals of the pyridine and of the bridging cyanide group, respectively.

In the Vis spectrum a pH dependent band appears. At pH from 5 to 9 it is situated at 470 nm and is attributed to the CT transition from the iron to the oxime nitrogen acceptor orbital. By increasing the pH from 9 to about 11, the band shifts to 520 nm. As in a report on the effect of pH on the complex of PA-2 and iron(II) ions [10] and another one on similar shifts connected with pH changes observed in the spectrum of the mononuclear $[Fe(CN)_4(pyCHNOH)]^{2-}$ ion [6], we have supposed that the observed colour change is a result of the deprotonation of the oxime group. Band positions and molar absorptivities of the binuclear and the constituent mononuclear complexes are summarized in Table 1.

IR data conform with the proposed structure of the complex. The intense broad band at 3400 cm^{-1} is due to hydration water. The cyanide stretching frequencies occur in the region 2130–2030 cm^{-1}. The strong bands at 2035 and 2060 cm^{-1} are assigned to the terminal cyanide groups, and the weak band located at 2130 cm^{-1}, which is absent in the spectrum of the mononuclear complex [6], is associated with the bridging cyanide group. Namely, the bridge formation is known to exhibit a shift of the cyanide stretching to higher frequencies [11, 12]. The C=N and N–O oxime stretching bands in the free ligand are affected upon complex formation in position and intensity, respectively. The ν(CN) band is shifted from 1597 to 1642 cm^{-1}. Such a change of the band position is due to conjugation which leads to stabilization. The high wavenumber of the band indicates that the undissociated oxime group is present in the complex [13]. The very strong band located at 978 cm^{-1} in the free ligand which is assigned to ν(NO) is nearly absent in the complex, which verifies metal oxime interaction and supports the assumption that the nitrogen atom of the oxime is coordinated to the iron. The pyridine ring stretching vibrations in the range 1600–1400 cm^{-1} are slightly blue shifted upon complex formation, which indicates that the pyridine nitrogen also participates in this interaction.

During this work we have found that mercury(II) ions catalyse the reaction between AmP and PA-2. Depending on the mercury(II) concentration, two distinct products can be formed. When the ratio of the concentrations of $HgCl_2$ and AmP is less than 1.5, the binuclear complex presented in this paper is formed. When the excess $HgCl_2$ is added in greater amounts, total decomposition of pentacyanoferrate(II) ions occurs, and a red complex is formed which corresponds to the tris-pyridine-2-aldoxime-iron(II) complex [10].

Because the uncatalysed reaction between AmP and PA-2 takes several days to reach equilibrium, the experiments were repeated, but with the addition of small amounts of $HgCl_2$. The stoichiometry of the complex at pH 6 and 10 was proved to be the same as in the experiments carried out without mercury(II), [AmP]:[PA-2] = 2:1, and the analysis of the product isolated at pH 6 also confirmed that the same complex is in question.

Such an influence of mercury(II) is contrary to the observed negative interference of Hg^{2+} on the formation of oximatopentacyanoferrate(II) complexes. On the other hand, it conforms with the fact that mercury(II) ions catalyse the reactions of pentacyanoferrate(II) ions with some bidentate ligands such as 2,2′-bipyridyl [14], 1,10-phenanthroline [14] and ferrozine [15], which result in the forma-

TABLE 1. Band positions and molar absorptivities of the binuclear and the constituent mononuclear complexes

Complex	λ_{max}(nm) [ϵ(M^{-1} cm^{-1})]			
	pH = 4–9			pH = 9–11
$[(CN)_5Fe\text{-}NC\text{-}Fe(CN)_3(pyCHNOH)]^{5-}$	340(1600)	396(2600)	470(2300)	520(1300)
$[(CN)_5Fe(NH_3)]^{3-}$		400(450)		
$[(CN)_4Fe(pyCHNOH)]^{2-}$	347(2300)[a]		473(5100)[a]	465(4800)[a,b]

[a] Values from ref. 6. [b] pH > 10.

tion of substituted tetracyanoferrate(II) complexes. The catalytic effect of Hg(II) ions can be explained by their great affinity for CN^- and ability to abstract cyanide ligands from the metal center where the linking of the oxime occurs.

In accordance with the collected data, we have concluded that in the reaction of pyridine-2-aldoxime and sodium amminepentacyanoferrate(II) under the conditions quoted a binuclear cyano-bridged complex is formed. Pyridine-2-aldoxime behaves as a bidentate chelating ligand, which binds to the metal ion through both nitrogen atoms, in accordance with the observed catalytic effect of mercury(II) ions.

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