The Pentacyanopyridine-4-aldoximeferrate(II) Ion Estimation of the Ligand's Coordination Site

N. Burger* and V. Hankonyi

Department of Chemistry and Biochemistry, Faculty of Medicine, University of Zagreb, 41000 Zagreb, Croatia

Summary. Pyridine-4-aldoxime reacts with the aquopentacyanoferrate(II) ion by forming a complex compound of 1:1 molar ratio. The pK_a value of the oxime group in the complex, the influence of pH changes on its formation as well as IR data indicate the coordination of pyridine-4-aldoxime through the pyridine nitrogen.

Keywords. Pentacyanopyridine-4-aldoximeferrate(II) ion; oxime, coordination site; Spectrophotometry.

Das Pentacyanopyridin-4-aldoximferrat(II)-Ion. Bestimmung der Koordinationsstelle

Zusammenfassung. Pyridin-4-aldoxim reagiert mit dem Aquopentacyanoferrat(II)-Ion und bildet einen Komplex mit dem Molarverhältnis 1:1. Der pK_a Wert der Oxim-Gruppe im Komplex, der Einfluß des pH auf seine Bildung, wie auch die IR Daten weisen auf die Koordination des Pyridin-4-aldoxim über den Pyridin-Stickstoff hin.

Introduction

The reactions between aldoximes of the pyridine and the pyridinium type and the aquopentacyanoferrate(II) ion (*AqP*) have been the subject of our investigations for several years [1–6]. They are relatively slow and very dependent on the pH and the ionic strength of the reaction medium. The replacement of the water molecule in the iron compound with the oximes produces intensely coloured complexes ($\lambda_{max} = 470$–570 nm) whose absorption maxima in very alkaline media shift bathochromically; in these complexes, the oximes are linked to the iron center through the oxime nitrogen. UV light was found to accelerate these reactions [7].

Pyridine-4-aldoxime (*PA-4*) behaves distinctly. It reacts quickly with *AqP*, forming a yellow compound whose absorption maximum is located at the low wavelength of 435 nm and is shifted hypsochromically in very alkaline media. The reaction is unaffected by ionic strength and by pH in the range from 5 to 9. The isolated reaction product was identified as sodium pentacyanopyridine-4-aldoximeferrate(II) hexahydrate [3]. The pK_a value of the oxime group in *PA*-4 is high (9.99) [8] in comparison with the pK_a values of the majority of the examined oximes ($pK_a \sim 8$), and the stability constant of the produced complex is greater

$(K = 2.1 \times 10^5 \, M^{-1})$. UV light was found to have a negative influence on this complex formation, i.e. irradiation results in its disintegration [7].

All these data refer to the coordination of *PA-4* through the pyridinic nitrogen. Because many oximes are effective antidotes against organophosphorus poisoning and their compounds with *AqP* as low-spin iron(II) complexes are simple models for studies of metal-ligand interactions in biological systems, we found it interesting to establish which one of its two nitrogens links *PA-4* to the iron in the complex compound.

Experimental Part

All reagents used were of analytical-reagent grade. Redistilled water was used throughout the experiments. Britton–Robinson buffers were prepared by mixing $100 \, cm^3$ of phosphoric, boric and acetic acid mixtures (all $0.04 \, M$) with different volumes of $0.2 \, M$ sodium hydroxide. A constant ionic strength of $0.1 \, M$ was obtained by adding sodium chloride.

Solutions of $Na_3[Fe(CN)_5OH_2]$ (*AqP*) were obtained by aquation of $Na_3[Fe(CN)_5NH_3] \cdot 3H_2O$, dissolving a "Touzart-Matignon" reagent in water 10 min before use. Pyridine-4-aldoxime was a "Fluka" reagent. It was recrystallized from water; m.p. 130 °C.

Measurement samples were prepared by mixing solutions of buffer or sodium hydroxide, sodium chloride, oxime, water and *AqP*. To determine the pK_a of the oxime group in the complex, a five-fold molar excess of the *AqP* over the oxime was applied when the absorbances were measured in the UV region, while a five-fold molar excess of the oxime was used when the absorbances were measured in the Vis region. Spectroscopic measurements were made with a UNICAM SP 600 UV spectrophotometer and 1-cm silica–glass cells. IR spectra were recorded in KBr pellets.

Results and Discussion

A preliminary attempt to establish the presence of either the free pyridinic or the oximic nitrogen in the isolated compound was made by spot-tests using Draggendorf's and $CuCl_2$ reagents [9]; they were unsuccessful, partly because of the yellow-orange colour of the sole complex.

The IR spectrum of the complex was recorded. The high degree of hydration and strong hydrogen bonding were considered to be responsible for the broadness and the intensity of the bands observed between 3500 and $2500 \, cm^{-1}$. Bands at

Table 1. Characteristic IR frequencies of the pyridine ring

ν (ring)/cm^{-1}	
Oxime	Complex
1573 w	1570 w
1520 w	1516 w
1508 w	1504 w
1488 w	1488 w
1425 m	1420 m
1410 m	1408 m

2150(w), 2110(m) and 2058(vs) cm^{-1} were assigned to cyanide stretchings. The two very strong bands at 1608 and 1625 cm^{-1} are the C=N (oxime) stretchings whose positions ($v > 1600$ cm^{-1}) indicate that the oxime proton is not heterolysed and a neutral oxime group is present in this complex [10]. The stretching bands associated with the pyridine ring for the free ligand and the oxime are given in Table 1. It is possible to assume that the effects of the π-back bonding from metal to ligand compensate the blue-shift effect on the bands which, therefore, do not suffer appreciable displacements. The very strong band at 992 cm^{-1} which is assigned to the NO group is unaffected upon complexation both in intensity and position; this fact indicates that the oxime group does not participate in complex formation. The band at 826 cm^{-1} refers to the *para*-position of the ligand oxime group.

The pK_a of the oxime group in the coordinated ligand was determined by spectrophotometric titration. In the UV region, two pH-dependent bands appear at 246 and 290 nm which are characteristic of intraligand absorptions. The band at 246 nm appears in neutral and slightly alkaline media. Addition of a strong base shifts the band to 290 nm with an isosbestic point at 266 nm. The measured absorbances were corrected for the contribution from the unreacted pentacyano-ferrate(II), whose equilibrium concentration was calculated from the previously quoted stability constant of the complex. A plot of the solution pH vs. the absorbances at the wavelengths of the respective maxima demonstrates the characteristic shape of a weak base titration curve and gives the pK_a value for the assumed equilibrium:

$$(CN)_5FeN-CH=NOH^{3-} + OH^- \rightleftharpoons (CN)_5FeN-CH=NO^{4-} + H_2O.$$
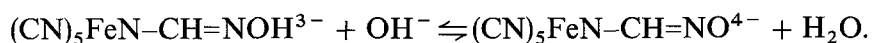
In the visible region, measurements were made at 460 nm at which the absorption contribution from the reactants can be neglected and the greatest difference between the absorbances of the protonated and unprotonated species (435 and 420 respectively) assigned to MLCT transitions is observed. The results from treatment of the MLCT or the intraligand region of the spectrum are essentially identical. A pK_a value of 10.60 ± 0.04 (24 °C), which is slightly different from that one of the oxime group in the free ligand, was calculated. A value of 10.6 has been recently obtained from kinetic measurements too [11].

When coordination occurs through the oxime group, its pK_a can change considerably. For example, in the tris-pyridinium-2-aldoxime-iron(II) complex, the pK_a of the coordinated oxime is more than three units lower than the pK_a of the free oxime [12], which conforms with the electrostatic effect of coordination, i.e. with σ-donation. The slight increase in the pK_a of the pyridine-4-aldoxime upon coordination can be assigned to errors made by maintaining and measuring pH values > 12 and to the increase of the ligand basicity due to the back-donation of electron density from the metal to the ligand. The existence of π-back bonding, i.e. orbitals overlap, can be verified by considering the pK_a value of the charge-transfer exited state, pK_a^*, which can be calculated from the equation [13]:

$$pK_a^* = pK_a(\text{gs}) + \frac{2.86(v_1 - v_2)}{2.3RT}$$

where $pK_a(\text{gs})$ is the ground state pK_a, v_1 is the frequency in wavenumbers of the MLCT absorption of the unprotonated form, and v_2 is the frequency of the MLCT

absorption of the protonated form. The obtained value of $pK_a^* = 12.32$ is greater than the determined pK_a(gs), i.e. the electron density increases in the exited state. Thus, this charge-transfer transition involves a transfer of electron density, presumably from the filled $t_{2g}d_\pi$ metal orbitals to the unoccupied lowest lying π^* orbital of the ligand. Spectral measurements made in strong acidic media have shown that at $pH < 4$ the complex is not formed at all. This happens because of the protonation of the pyridine nitrogen ($pK_a = 4.77$ at $20\,°C$) which prevents its coordination.

In conclusion, the pK_a value of the oxime group in the pentacyanopyridine-4-aldoximeferrate(II) ion, the influence of acid pH on its formation, as well as IR data and previous evidence about this complex indicate the coordination of pyridine-4-aldoxime through the pyridine nitrogen.

References

[1] Karas-Gašparec V., Weber K. (1968) Z. Phys. Chemie (Leipzig) **237**: 235
[2] Hankonyi V., Ondrušek V., Karas-Gašparec V., Binenfeld Z. (1972) Z. Phys. Chemie (Leipzig) **251**: 280
[3] Burger N., Karas-Gašparec V. (1981) Talanta **28**: 326
[4] Burger N., Karas-Gašparec V. (1984) Talanta **31**: 169
[5] Burger N., Hankonyi V., Smerić Z. (1989) Inorg. Chim. Acta **165**: 83
[6] Burger N., Hankonyi V., Smerić Z. (1990) Z. Phys. Chemie (Leipzig) **271**: 787
[7] Burger N., Hankonyi V. (1992) Anal. Lett. **25**: 7
[8] Mason S. F. (1960) J. Chem. Soc.: 22
[9] Stahl E. (1969) Thin-Layer Chromatography, Springer, Berlin Heidelberg New York, pp. 865, 874
[10] Krause R. A., Colthup N. B., Busch D. H. (1961) J. Phys. Chem. **65**: 2216
[11] Alonso A. M., Williams P. A. M., Aymonino P. J. (1988) Anal. Asoc. Quim. Argent. **76**: 151
[12] Hanania G. I. H., Irvine D. H. (1962) J. Chem. Soc.: 2745
[13] Johnson C. R., Shepherd R. E. (1983) Inorg. Chem. **22**: 1117