

The *tris*(2-Nitroso-1-naphtholato)ferrate(II) Ion

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Summary. The *tris*(2-nitroso-1-naphtholato)ferrate(II) complex is isolated in the form of its ferrous salt and characterized by analytical, infrared, and UV/Vis data. In the solid state and in solution the complex has predominantly a quinone oximic structure. The oxime group is deprotonated and bound to iron *via* the nitrogen atom.

Keywords. Aquapentacyanoferrate(II); Iron(II); 2-Nitroso-1-naphthol; Spectroscopy.

Das *tris*(2-Nitroso-1-naphtholato)ferrat(II)-Ion

Zusammenfassung. Der *tris*(2-Nitroso-1-naphtholato)ferrat(II)-Komplex wurde in der Form seines Ferrosalzes isoliert und durch Analyse und Spektroskopie (IR, UV/Vis) charakterisiert. Im festen Zustand und in Lösung hat der Komplex vorwiegend Chinonoximstruktur. Die Oximgruppe ist deprotoniert und über das Stickstoffatom an das Eisen gebunden.

Introduction

The reaction of 2-nitroso-1-naphthol with the aquapentacyanoferrate(II) ion (*AqP*) has been studied recently [1]. In the first step of the reaction, a substitution process leads to the formation of the 2-nitroso-1-naphtholatopentacyanoferrate(II) ion, probably by a dissociative mechanism [2]. In the second step, an additional replacement of a cyanide group from the metal center leads to a tetracyanoferrate(II) species of binuclear type, pentacyanoferrate(II)- μ -cyano-tricyanonitrosonaphtholatoferrate(II). It was found that mercury(II) ions catalyze the latter reaction, provided $[\text{Hg}^{2+}] < 0.5 \cdot [\text{AqP}]$. If mercury(II) ions were added in higher amounts, further decomposition of the cyanoferrate(II) species occurred, leading to a new complex which has been proposed to be the *tris*(2-nitroso-1-naphtholato)ferrate(II) ion. In order to prove this assumption, the complex has been prepared [1].

Although many reports appeared in the literature about the product formed by the reaction of iron(II) and 1-nitroso-2-naphthol [3, 4], surprisingly little attention was paid to the reaction of the same metal ion with the isomeric 2-nitroso-1-naphthol [5]. In this paper, a reproducible preparation of the *tris*(2-nitroso-1-naphtholato)ferrate(II) is described, using *Mohr's* salt instead of the less convenient iron(II) perchlorate. UV/Vis and IR characteristics of the complex are presented along with a comparative discussion regarding the complexes achieved in the reaction of the same ligand with the aquapentacyanoferrate(II) ion.

Results and Discussion

2-Nitroso-1-naphthol reacts with the ferrous ion to form a green complex within a few minutes. The formation of the complex is considerably influenced by the pH value and the ionic strength of the reaction mixture. Maximum absorbances were obtained at pH values from 5 to 6; increased ionic strengths were found to decrease the absorbance. The composition of the complex was determined by the method of continuous variations [6, 7] and by the molar ratio method [8] and was found to be $1 \text{ Fe}^{2+} : 3 \text{ nitrosonaphthols}$. Because of the high stability constant of the complex, the same methods were suitable for its calculation, and a value of $\log K = 13.88 \pm 0.07$ was obtained at 24°C and $pH = 6$ as the mean value of nearly equal results deduced according to both procedures. The complex was isolated from a solution containing 2-nitroso-1-naphthol and iron(II) ions in a 3:1 molar ratio. The ligand is deprotonated and bound as an anionic moiety, which is also the case in other metal chelates of 2-nitroso-1-naphthol [3].

The UV spectrum of an ethanolic solution of the complex resembles closely that of 2-nitroso-1-naphthol in alkaline medium [9, 10]. Both maxima appearing at 292 nm ($\epsilon = 71600 \text{ M}^{-1} \cdot \text{cm}^{-1}$) and 337 nm ($\epsilon = 50000 \text{ M}^{-1} \cdot \text{cm}^{-1}$) are due to ligand absorptions and are characteristic of the *ortho*-quinone oxime system [9]. In the visible region, the band at 440 nm ($\epsilon = 23200 \text{ M}^{-1} \cdot \text{cm}^{-1}$) has been assigned to the ligand's charge resonance [11], whereas the broad band situated around 700 nm ($\epsilon = 23400 \text{ M}^{-1} \cdot \text{cm}^{-1}$) is characteristic of the complex and is attributed to the iron-to-ligand CT transition.

The IR spectrum of *tris*(2-nitroso-1-naphtholato)ferrate(II) is presented in Fig. 1 together with the spectrum of pentacyanoferrate(II)- μ -cyano-tricyano-2-nitroso-1-

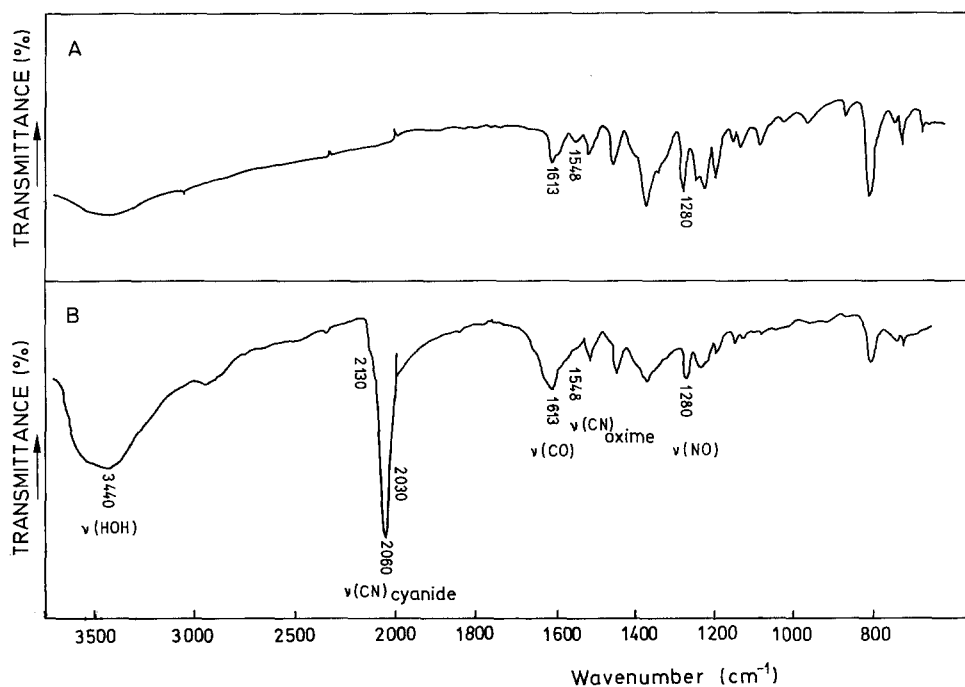


Fig. 1. IR spectra of (A) $\text{Fe}[\text{Fe}(\text{C}_{10}\text{H}_6\text{O}_2\text{N}_3)_2]$ and (B) $\text{Na}_6[\text{Fe}_2(\text{CN})_9(\text{C}_{10}\text{H}_6\text{O}_2\text{N})] \cdot 12\text{H}_2\text{O}$

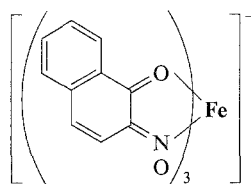


Fig. 2. Representation of the $[\text{Fe}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_3]^-$ species

naphtholtoferrate(II) which has been interpreted in detail earlier [1]. Except for the cyanide stretchings ($\nu = 2130\text{--}2030\text{ cm}^{-1}$) and the band at 3440 cm^{-1} due to lattice water in the spectrum of the latter, they are basically identical. The shifts and attenuations of the $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{N})_{\text{oxime}}$, and $\nu(\text{NO})$ bands in comparison with their position in the free ligand [12, 13] ($\nu(\text{C}=\text{O}) = 1660\text{ cm}^{-1}$, $\nu(\text{C}=\text{N})_{\text{oxime}} = 1548\text{ cm}^{-1}$, $\nu(\text{NO}) = 1060\text{ cm}^{-1}$) prove that both the carbonyl and the oxime group participate in the complex formation, whereas the high position of the $\nu(\text{NO})$ frequency indicates that the nitrogen atom of the deprotonated oxime group coordinates to the metal center [14, 15]. This is also the case in iron chelates of similar nitroso compounds [4, 16]. A representation of the proposed structure is given in Fig. 2.

The actual results offer evidence that 2-nitroso-1-naphthol is bound to iron in an analogous way both in tris(2-nitroso-1-naphtholato)ferrate(II) and in pentacyanoferrate(II)- μ -cyano-tricyano-2-nitroso-1-naphtholtoferrate(II).

Experimental

All chemicals used were of reagent grade. Redistilled water was used throughout. Britton and Robinson buffers were prepared by mixing 100 cm^3 of a mixture of phosphoric, boric, and acetic acid (all 0.04 M) with different volumes of 0.20 M sodium hydroxide. 2-Nitroso-1-naphthol was purchased from Fluka. It was recrystallized from water (m.p.: $142\text{--}144\text{ }^\circ\text{C}$), and its solutions were prepared in ethanol or methanol. Mohr's salt, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$, was purchased from Kemika. Sodium chloride was used to maintain a constant ionic strength of 0.05 M .

The complex was generated in solutions to be spectrophotometrically examined (10% ethanol-water v/v) by mixing 2 cm^3 of buffer, 2-nitroso-1-naphthol, sodium chloride, ethanol, Mohr's salt and water to produce a total volume of 5 cm^3 .

The preparation of the complex was carried out as follows: 5 cm^3 of a methanolic solution containing 0.058 g (0.33 mmol) of 2-nitroso-1-naphthol were added to 3 cm^3 of an aqueous solution of 0.044 g (0.11 mmol) of Mohr's salt. The resulting mixture was cooled at $0\text{ }^\circ\text{C}$ for 30 min. The precipitated dark-green solid was filtered off, washed with water and small portions of ethanol, and dried *in vacuo* over phosphorus pentoxide. It was found to be anionic by treatment with an DEAE-Sephadex A-35 anion exchanger. Iron was determined as Fe_2O_3 . Found: C, 59.9; H, 3.2; N, 7.0; Fe, 14.2%; calc. for $\text{Fe}[\text{Fe}(\text{C}_{10}\text{H}_6\text{NO}_2)_3]_2$: C, 60.0, H, 3.0; N, 7.0; Fe, 14.0%.

Spectroscopic measurements were performed by an UNICAM SP 600 UV spectrophotometer in 1 cm silica glass cells. IR spectra were recorded as KBr pellets.

References

- [1] Foretić B, Burger N, Hankonyi V (1995) *Polyhedron* **14**: 605
- [2] Stochel G, Chatlas J, Martinez P, van Eldik R (1992) *Inorg Chem* **31**: 5480
- [3] Chakravorthy A (1974) *Coord Chem Rev* **13**: 17
- [4] Charalambous J, Frazer MJ, Sims R (1976) *Inorg Chim Acta* **18**: 247

- [5] Allen DK, Charalambous J, Johri MH, Sims R, Bailey J, Mathewson HD, Cunningham D (1978) *Inorg Chim Acta* **29**: L235
- [6] Job P (1928) *Ann Chim* **9**: 113
- [7] Vosburgh WC, Cooper GR (1941) *J Am Chem Soc* **63**: 437
- [8] Harvey AE, Manning DL (1950) *J Am Chem Soc* **72**: 4488
- [9] Burawoy M, Cais M, Chamberlain JT, Liversedge F, Thompson AR (1955) *J Chem Soc* 3727
- [10] Gurrieri S, Siracusa G (1971) *Inorg Chim Acta* **5**: 650
- [11] Chatterjee KK (1959) *Anal Chim Acta* **20**: 423
- [12] Hadži D (1956) *J Chem Soc* 2725
- [13] Barbalat YA, Peshkova VM (1970) *Vestn Mosk Univ Khim* **11**: 441
- [14] Constantino VR, Toma HE, Oliveira LFC, Santos P (1992) *J Raman Spectrosc* **23**: 629
- [15] Natarajan C, Nazeer Hussain A (1983) *Indian J Chem* **22A**: 527
- [16] Barjesteh H, Charalambous J, Pathirana ND (1993) *Polyhedron* **12**: 883

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