

The Negative Ions' Mass Spectrum of tris(2-Nitroso-1-naphtholato)ferrate(II)

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The product of the examined reaction of Fe^{2+} and 2-nitroso-1-naphthol was confirmed to be the earlier assumed tris(2-nitroso-1-naphtholato)ferrate(II) by mass spectrometry.

Key words: mass spectrometry, the tris(2-nitroso-1-naphtholato)ferrate(II) ion

INTRODUCTION

2-Nitroso-1-naphthol is currently used as a complexing agent in cobalt analysis.^{1,2} It is also a sensitive and specific histochemical reagent for fluorimetric determinations of tyrosine residues in proteins and peptides.³ Along with other phenols and naphthols, it belongs to biologically important compounds, especially because of its cytotoxic action.⁴

Although there has been considerable interest in iron(II) complexes of 1-nitroso-2-naphthol,^{1,5} surprisingly little work was carried out on chelate complexes of the same metal ion with the isomeric 2-nitroso-1-naphthol. Earlier, the structure of the iron(II) complex of 2-nitroso-1-naphthol was investigated using magnetochemical and Mössbauer spectroscopic techniques.⁶ The authors suggested the existence of a complex of composition $1 \text{ Fe}^{2+} : 2$ nitrosonaphthols with an oligomeric structure, which was prepared by mixing ferrous ammonium sulphate and 2-nitroso-1-naphthol in a 1 : 2 molar ratio.

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The complex was found to add two moles of pyridine to give a product of the formula $\text{Fe}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2 \times 2\text{C}_5\text{H}_5\text{N}$.

As a continuation of our studies on complexes of nitrosonaphthols, we have also investigated the reaction between the iron(II) ion and 2-nitroso-1-naphthol, but the reaction product was isolated from a solution containing iron(II) ions and 2-nitroso-1-naphthol in a 1 : 3 molar ratio. The characteristics of the complex and the optimum conditions for its formation have been described.^{7,8} Although the composition of the complex in solution was found by spectrophotometric methods to be 1 Fe^{2+} : 3 nitrosonaphthols, a certain doubt remained about its formula since the results of quantitative analysis of the isolated compound conform equally with $\text{Fe}[\text{Fe}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_3]_2$ and $\text{Fe}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2$. (The ratio of the metal toward the ligand is the same in both formulas). The aim of this work was to establish which of the two formulas is the correct one, which has been done by mass spectrometry.

EXPERIMENTAL

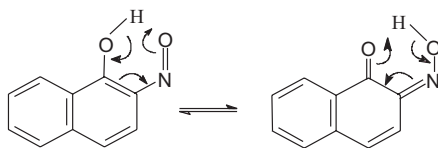
All the chemicals used were of reagent grade. Redistilled water was used throughout. 2-Nitroso-1-naphthol was a Fluka Chemie AG (Buchs, Switzerland) reagent, further purified by recrystallisation from water (m.p. 142–144 °C). Mohr's salt, $(\text{NH}_4)_2\text{SO}_4 \times \text{FeSO}_4 \times 6\text{H}_2\text{O}$, was purchased from Kemika (Zagreb, Croatia) while $\text{Fe}(\text{ClO}_4)_2 \times 6\text{H}_2\text{O}$ was synthesized by a known procedure.⁹

The tris(2-nitroso-1-naphtholato)ferrate(II) complex was prepared by mixing methanolic solutions of 2-nitroso-1-naphthol with a methanolic solution of $\text{Fe}(\text{ClO}_4)_2 \times 6\text{H}_2\text{O}$ or a water solution of Mohr's salt in a 3 : 1 molar ratio. The precipitated dark-green solid was filtered off, washed with small portions of water and ethanol and dried *in vacuo* over phosphorus pentoxide. It was found to be anionic by treatment with a DEAE-Sephadex A-35 anion exchanger. Iron was determined as Fe_2O_3 . *Anal.* Calcd. for $\text{Fe}[\text{Fe}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_3]_2$: C 60.03, H 3.02, N 7.00, Fe 13.95%; found: C 59.94, H 3.28, N 6.85, Fe 14.36% and C 59.85, H 3.19, N 6.95, Fe 14.20% using ferrous perchlorate and Mohr's salt, respectively.

The mass spectrum was recorded at the Ruđer Bošković Institute on an Extrel FTMS 2001-DD Fourier transform spectrometer using the direct laser desorption/ionization technique. A few micrograms of the isolated compound was dissolved in ethanol and the solution was allowed to evaporate on the stainless steel disk of the direct-insertion probe. A pulsed Nd : YAG laser (moderated at the 1065 nm wavelength) Quanta Ray DCR-11 was used to desorb/ionize the solid.

RESULTS AND DISCUSSION

Ortho-substituted nitrosonaphthols can undergo tautomerisation to give oxo-oximes:



In the case of 2-nitroso-1-naphthol, the equilibrium is greatly displaced toward the keto-form and the compound has, in solid state and in solution, a predominately quinone-oximic structure.⁸ The product of the reaction of 2-nitroso-1-naphthol (also referred to as 1,2-naphthoquinone-2-oxime) and the Fe^{2+} ion is identical to the one which forms in the second stage of the reaction between the same ligand and the aquapentacyanoferrate(II) ion in the presence of Hg^{2+} , provided the concentration ratio of Hg^{2+} ions toward aquapentacyanoferrate(II) is greater than 2 (Ref. 8). It was assumed to be the tris(2-nitroso-1-naphtholato)ferrate(II) ion, a green complex ($\lambda_m = 700$ nm, $K_{\text{stability}}(24^\circ\text{C}) = 7.58 \times 10^{13} \text{ M}^{-3}$, $\epsilon = 23400 \text{ M}^{-1} \text{ cm}^{-1}$)^{7,8} where the ligand binds to iron as an anionic moiety, which is also similar to other metal chelates of 2-nitroso-1-naphthol¹ and other nitroso compounds.^{10,11} To prove the correct-

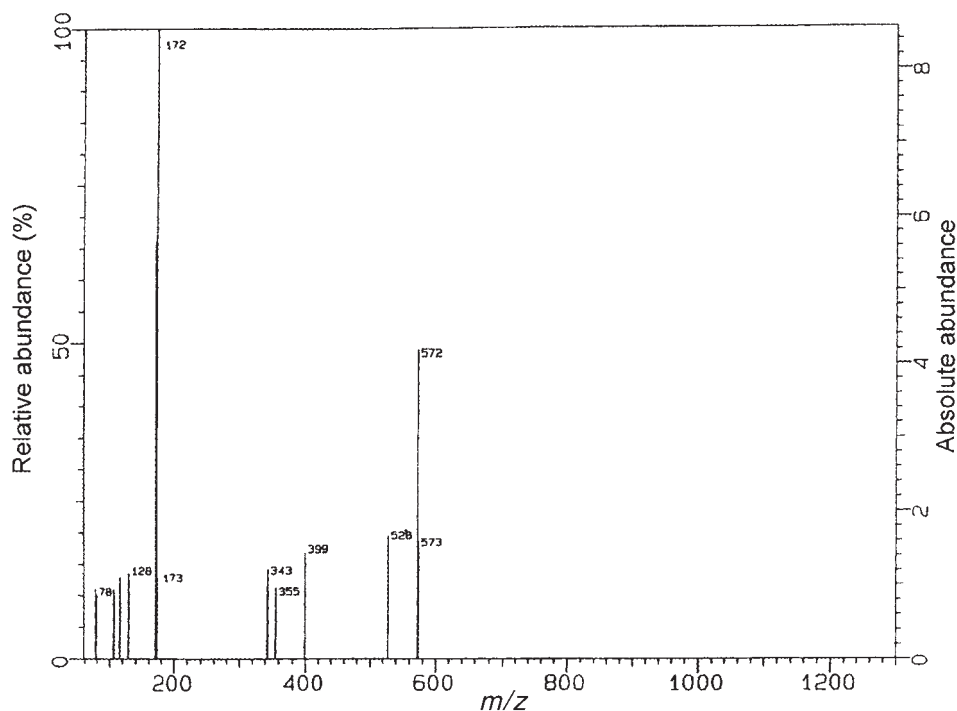


Figure 1. The LD FTMS spectrum of the negative ions of complex $\text{Fe}[\text{Fe}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_3]_2$.

TABLE I
Major ions in the mass spectrum of the
tris(2-nitroso-1-naphtholato)ferrate(II) complex

m/z	Assignment
572	$[\text{Fe}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_3]^-$
528	$[\text{Fe}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_3 - \text{CO} - \text{O}]^-$
399	$[\text{Fe}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2 - \text{H}]^-$
355	$[\text{Fe}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2 - \text{H} - \text{CO} - \text{O}]^-$
172	$[\text{C}_{10}\text{H}_6\text{O}_2\text{N}]^-$

ness of the above assumption, the mass spectrum of the isolated compound was recorded and is presented in Figure 1. The characteristic fragments in the spectrum are described in Table I. The peak at 572 m/z provides convincing evidence for the presence of the tris(2-nitroso-1-naphtholato)ferrate(II) ion. Peaks arising from associated complexes earlier observed in the mass spectra of related compounds¹² were of extremely low relative abundances (2–3%) and were not found. Additional fragmentations are due to the loss of O, CO and the ligand from the complex. A similar fragmentation pattern was found in the mass spectrum of the nickel(II) complex of 2-nitroso-1-naphthol¹² and confirms the earlier statement deduced from IR data that the deprotonated oxime group coordinates to the metal centre through the nitrogen atom.⁷

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SAŽETAK**Maseni spektar negativnih iona kompleksa
tris(2-nitrozo-1-naftolato)ferata(II)**

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Produkt ispitivane reakcije željezova(II) iona i 2-nitrozo-1-naftola jest tris(2-nitrozo-1-naftolato)ferat(II) što je potvrđeno masenom spektrometrijom.