

“Brown-Ring”-Related Coordination Polymers of the Quartet- $\{\text{FeNO}\}^7$ Chromophore

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Dedicated to Professor Manfred Scheer on the Occasion of his 65th Birthday

Abstract. A conspicuous detail of the so-called brown-ring test (the analytical test on nitrate) is the reddish color of the bottom layer of concentrated sulfuric acid, which develops upon the bleeding of the brown layer into the acid. Crystals of the same color form from a solution of ferrous sulfate in concentrated sulfuric acid on saturation with gaseous nitric oxide. The structure of this $\text{H}_2\text{O}[\{\text{Fe}(\text{NO})(\mu_4\text{-SO}_4)(\mu_2\text{-SO}_4)_{0.5}\}_{n/m}]$ (**1a**) is made up from infinite chessboard-type layers with sulfur on the field junctions and $\text{Fe}(\text{NO})$ moieties below the black

and above the white fields. An Fe–N–O angle of about 160° causes disorder in the tetragonal space group $I4/mmm$. A similar crystal pathology was found in the related $[\{\text{Fe}(\text{MeOH})(\text{NO})(\mu_4\text{-SO}_4)\}_{n/m}]$ (**1b**) in the same crystal class. A one-dimensional coordination polymer is formed in crystals of a third compound that comprises the $\text{Fe}(\text{NO})\text{O}_5$ coordination pattern, namely the brown oxalato species $[\{\text{Fe}(\text{H}_2\text{O})(\text{NO})(\mu_2\text{-ox})\}_{n/m}\cdot\text{H}_2\text{O}]$ (**2**). A still larger NO tilt of about 156° is not obscured by disorder in the triclinic crystals of **2**.

Introduction

In a first intense period of research on the reaction products of iron(II)-containing solutions and gaseous nitric oxide, the competing groups of *Manchot* and *Kohlschütter* discovered experimental conditions for the preparation of the parent chromophore $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$ as well as variants thereof.^[1] In terms of color, weakly acidic $\text{Fe}^{\text{II}}/\text{NO}$ solutions containing this ion resemble the brown part of the layer, which is obtained in the course of a positive nitrate test in the classical “brown-ring” test.

Few crystalline solids had been reported in the publications of that time. In particular, *Manchot* claimed two solids: a brown to black $2\text{FeSO}_4\cdot\text{NO}\cdot 13\text{H}_2\text{O}$, which precipitated from aqueous solutions of the components on ethanol addition, and red crystals of an $\text{FeSO}_4\cdot\text{NO}$, which grew from red solutions of ferrous sulfate in concentrated sulfuric acid after exposure to nitric oxide.^[1e] *Schlesinger* and *Salathe* reproduced *Manchot*'s red solutions and considered them identical with *Raschig*'s “ferrous nitrosulfonate”.^[2] We and others were not able to reproduce brown crystals of the claimed formula.^[3] However, the formation of red crystals from concentrated sulfuric acid reliably occurred as described by *Manchot*. It should be noted at this point that *Manchot*'s attention was drawn to

$\text{Fe}^{\text{II}}/\text{NO}$ solutions in concentrated sulfuric acid by a peculiarity of the nitrate test. Thus, Figure 1 of reference^[3a,3b] shows the typical cherry-red color when the ring's brown component bleeds into the bottom layer of concentrated acid.

In this work, we report on the composition and structure of *Manchot*'s red crystals. After having demonstrated their polymeric nature, we will extend our discussion to a related coordination polymer where the sulfate was replaced by oxalate. Both substances extend the rather limited class of quartet- $\{\text{FeNO}\}^7$ compounds with an $\text{Fe}(\text{NO})\text{O}_5$ chromophore, that is, a class with the brown-ring cation $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$ as the parent species.^[3a,3b] (Note the Enemark–Feltham notation, where the superscript “7” is the sum of the central metal's d-electrons and the nitrosyl ligand's π^* electrons; here, d^6 ferrous centers reacted with a neutral NO molecule, hence, $6 + 1 = 7$.)

Results and Discussion

$(\text{H}_2\text{O})[\{\text{Fe}(\text{NO})(\mu_4\text{-SO}_4)(\mu_2\text{-SO}_4)_{0.5}\}_{n/m}]$ (**1a**)

Following *Manchot*'s recipe, red, highly reactive crystals were obtained by the reaction of a ferrous-sulfate solution in concentrated sulfuric acid with nitric oxide gas at ambient temperature.^[1e] The solutions turned red immediately on contact to NO and, as reported by *Manchot*, large red crystals formed in the course of some hours.

At this point, it may be noted that our scientific ancestors fostered a rather poetical language in their publications. Thus, *Manchot* described these crystals with the words: “[The precipitate] consists of small, crimson, rather thick platelets, which keel over in the heavy liquid like floundering ice floes, and thus, contingent upon the position, from which they are beheld, appear as platelets or, when their narrow darker edge is turned upward, needle-shaped.” (Translation of *Manchot*'s “[Der Niederschlag] besteht aus kleinen, rothen, ziemlich

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dicken Krystallblättchen, welche in der schweren Flüssigkeit ähnlich wie Eisschollen umkippen und sich herumwälzen und daher je nach der Lage, in der man sie erblickt, als Blättchen oder, wenn die schmale dunklere Kante nach oben gerichtet ist, nadelartig erscheinen.”)

Crystal-structure analysis in the tetragonal space group $I4/mmm$ revealed a two-dimensional coordination polymer of the $\text{Fe}(\mu_4\text{-SO}_4)(\text{NO})$ part (Figure 1). The layers extend perpendicularly to the fourfold axis in the $(x\ y\ 1/4)$ plane. They may be described as a chessboard arrangement with the sulfato ligands on the junctions and $\text{Fe}(\text{NO})$ moieties above the black and below the white fields. The positional disorder of the nitrosyl ligand's oxygen atoms is distinct and could be resolved by a split model. As a result, Figure 2 shows one of the components and highlights the obvious tilt of the FeNO group. Notably, the tilt angle of about 164° is close to the value in crystals of the parent aqua cation.^[3a,3b] The space between the $\text{Fe}(\mu_4\text{-SO}_4)(\text{NO})$ layers is heavily disorderd. O3 in Figure 2 and a symmetry-generated counterpart in the layer below belong to a μ_2 -bridging sulfate, whose remaining SO_2 part is eightfold disorderd with all the atoms in the $(x\ y\ 0)$ plane. Finally, residual electron density in the same $(x\ y\ 0)$ plane was assigned to a disorderd oxonium ion. Since the positions of the hydrogen atoms were inaccessible, our interpretation of a $\text{H}_3\text{O}^+/\mu_2\text{-SO}_4^{2-}$ couple might read $\text{H}_2\text{O}/\mu_2\text{-HSO}_4^-$.

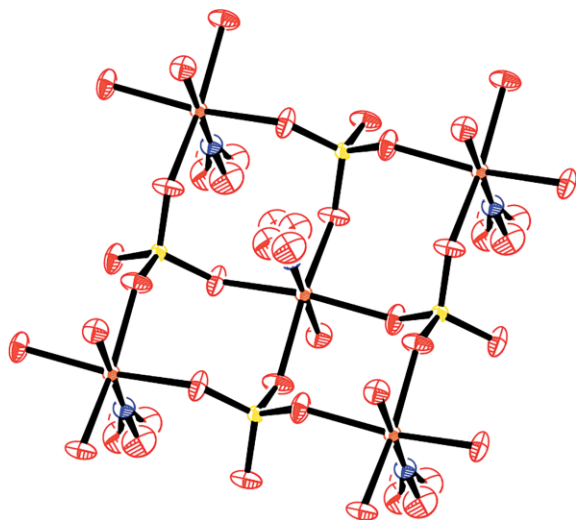


Figure 1. The two-dimensional $\{\text{Fe}(\text{NO})(\mu_4\text{-SO}_4)\}$ network, highlighting the fourfold disorder of the nitrosyl ligands about the space group's fourfold axis.

Two points regarding *Manchot's* experiments should be mentioned. First, *Manchot* himself, published the simple formula $\text{FeSO}_4\cdot\text{NO}$ for **1a**. Adopting this notation, **1a** may be reformulated as $\text{FeSO}_4\cdot\text{NO}\cdot\frac{1}{2}\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$. We may assume that he attempted to analyze the red crystals. However, given a sulfuric-acid- and water-containing solid, *Manchot* might have assumed to have a solid in his hands with adhering solvent.

Second, the preparation of cherry-red solutions could also start from iron(III) sulfate in concentrated sulfuric acid.^[1d] In this case, the double molar amount of nitric oxide was spent. On dilution, the red solutions decomposed and the ferric pre-

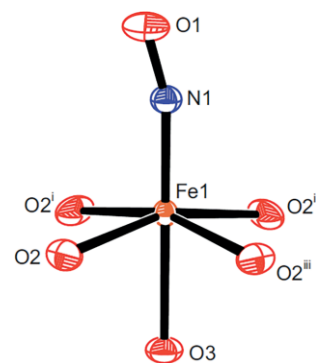


Figure 2. The coordination sphere about the $\text{Fe}(\text{NO})$ moiety in the red crystals of **1a** (40% probability ellipsoids). Distances in Å and angles in degrees: Fe1 to: N1 1.776(6), O2 2.073(3), O3 2.136(5); N1–O1 1.172(15), Fe1–N1–O1 164(2). Symmetry code: ⁱ $y, -x, z$; ⁱⁱ $-x, -y, z$; ⁱⁱⁱ $-y, x, z$.

cursor was recovered – unlike the decomposition of the red solution of ferrous sulfate in concentrated acid, which yielded the ferrous precursor. *Manchot* interpreted the recovery of the proper iron precursors as two different nitrosyl-iron compounds, the abovementioned $\text{FeSO}_4\cdot\text{NO}$ in the ferrous system and an iron(III) nitrosyl, $\text{Fe}_2(\text{SO}_4)_3\cdot 4\text{NO}$ in the ferric one.^[1d]

This latter assumption is not supported by our present-day knowledge. The capability of NO to reduce and nitrosylate ferric precursors to ferrous products has meanwhile been proved.^[4] The respective reaction equation, formulated as an equilibrium, is:



The actual progress of the reaction depends on the solvent. In the case of organic media, which react with the co-product NO^+ in a well-defined way, $\text{Fe}(\text{NO})^{2+}$ -type species were obtained in practically quantitative yield in an irreversible reaction. Examples include the use of alcohols, which form alkyl nitrites as the by-products.^[4a] However, concentrated sulfuric acid is a well controllable solvent for this particular system despite its high reactivity in general. The reason is its ability to simply dissolve salts of the nitrosyl cation such as nitrosyl hydrogensulfate without further transformation.^[5] Moreover, different from organic media, the reaction formulated above is a true equilibrium in $\text{H}_2\text{SO}_4(\text{conc.})$, thus restoring the ferric precursor on shifting it to the left, for example, by dilution with water – that was the course of events *Manchot* obviously observed. Thus, aqueous solutions are inappropriate for this reaction since, in a first step, NO^+ is transformed there according to $\text{NO}^+ + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{H}^+$. Nitrous acid then acts as an oxidant for any iron(II) species in the acidic solution, which restores the iron(III) state and NO. (It should be noted that this reaction is followed by $\text{Fe}(\text{NO})^{2+}$ formation in the course of the analytical nitrite test since iron(II) excess has to be assured there.)



Due to the H_3O^+ counterion, **1a** was a reactive solid, which decomposed rapidly in air. We, thus, tried to obtain the 2D

test on nitrate, similar but non-polymeric species seem to prevail in the concentrated acid of this compartment. We could assume, the bridging sulfato ligands of the solid might be replaced by terminal hydrogensulfato ligands.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1973267 (**1a**), CCDC-1973268 (**1b**), and CCDC-1973269 (**2**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

Supporting Information (see footnote on the first page of this article): Preparation of **1** and **2**, Mößbauer spectrum of **1b**, and selected X-ray data.

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