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"Brown-Ring"-Related Coordination Polymers of the Quartet-{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 $H_3O[{Fe(NO)(\mu_4-SO_4)}]$ (μ_2 -SO₄)_{0.5} $_{n/n}$] (**1a**) is made up from infinite chessboard-type layers with sulfur on the field junctions and Fe(NO) moieties below the black

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 $[Fe(H_2O)_5(NO)]^{2+}$ as well as variants thereof.^[1] In terms of color, weakly acidic Fe^{II}/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 2FeSO₄·NO·13H₂O, which precipitated from aqueous solutions of the components on ethanol addition, and red crystals of an FeSO₄·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 nitrosisulfonate".^[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

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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 [{Fe(MeOH)(NO)(μ_4 -SO₄)}_{*n/n*}] (**1b**) in the same crystal class. A one-dimensional coordination polymer is formed in crystals of a third compound that comprises the Fe(NO)O₅ coordination pattern, namely the brown oxalato species [{Fe(H₂O)(NO)(μ_2 -ox)}_{*n/n*}·H₂O] (**2**). A still larger NO tilt of about 156° is not obscured by disorder in the triclinic crystals of **2**.

 Fe^{II}/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-{FeNO}⁷ compounds with an Fe(NO)O₅ chromophore, that is, a class with the brown-ring cation $[Fe(H_2O)_5(NO)]^{2+}$ as the parent species.^[3a,3b] (Note the Enemark–Feltham notation, where the superscript "7" is the sum of the central metal's delectrons and the nitrosyl ligand's π^* electrons; here, d⁶ ferrous centers reacted with a neutral NO molecule, hence, 6 + 1 = 7.)

Results and Discussion

$(H_3O)[\{Fe(NO)(\mu_4 - SO_4)(\mu_2 - SO_4)_{0.5}\}_{n/n}] \ (1a)$

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 Fe(μ_4 -SO₄)(NO) part (Figure 1). The layers extend perpendicularly to the fourfold axis in the $(x y \frac{1}{4})$ plane. They may be described as a chessboard arrangement with the sulfato ligands on the junctions and Fe(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 $Fe(\mu_4-SO_4)(NO)$ 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 SO₂ part is eightfold disordered 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 disordered oxonium ion. Since the positions of the hydrogen atoms were inaccessible, our interpretation of a H_3O^+/μ_2 - SO_4^{2-} couple might read H_2O/μ_2 - HSO_4^{-} .

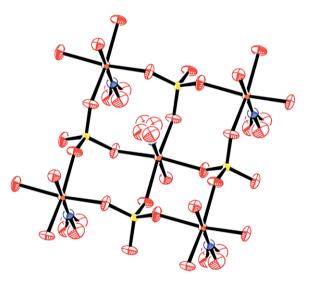


Figure 1. The two-dimensional $\{Fe(NO)(\mu_4-SO_4)\}$ network, highlighting the fourfold disorder of the nitrosyl ligands about the space group's fourfold axis.

Two points regarding *Manchot's* experiments should be mentioned. First, *Manchot* himself, published the simple formula $FeSO_4$ ·NO for **1a**. Adopting this notation, **1a** may be reformulated as $FeSO_4$ ·NO· $\frac{1}{2}H_2SO_4$ ·H₂O. 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-

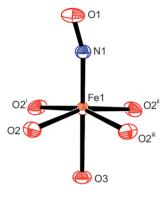


Figure 2. The coordination sphere about the Fe(NO) moiety in the red crystals of **1a** (40% probability ellipsoids). Distances in Å and angles in degrees: Fe1 to: N1 1.776(6), O2 2.073(3), O3 2.136(5); N1–O1 1.172(15), Fe1–N1–O1 164(2). Symmetry code: ⁱ y, -x, z; ⁱⁱ -x, -y, z; ⁱⁱⁱ -y, x, z.

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 $FeSO_4$ ·NO in the ferrous system and an iron(III) nitrosyl, $Fe_2(SO_4)_3$ ·4NO 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:

 $Fe^{3+} + 2NO \rightleftharpoons Fe(NO)^{2+} + NO^{+}$

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, Fe(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 $H_2SO_4(conc.)$, 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 NO⁺ + H₂O \rightarrow HNO₂ + 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 Fe(NO)²⁺ formation in the course of the analytical nitrite test since iron(II) excess has to be assured there.)

$[{Fe(CH_3OH)(NO)(\mu_4-SO_4)}_{n/n}]$ (1b)

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

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network of 1a free of reactive components. In fact, a red, and more robust solid was obtained from solutions containing ferrous and sulfate ions in wet methanol. On reaction with gaseous nitric oxide, the solutions turned green and tiny red crystals precipitated. In order to obtain crystals of sufficient size for single-crystal X-ray work, citric acid was added as a weakly bonding ligand to Fe²⁺ in the hope that the nucleation of too many seeds might have been retarded to some extent. In fact, larger crystals grew on citrate addition. However, again, disorder in a highly symmetric space group, here P4/nmm (used with origin choice 2), impaired the analysis. Notably, the same 2D pattern of the Fe(NO)(μ_4 -SO₄) part of the red solid [{Fe(MeOH)(NO)(μ_4 -SO₄)}_{n/n}] (1b) reveals itself in almost equal lattice constants a in **1a** and **1b**. The packing type as well as the *trans* ligand differ between 1a and 1b. In the latter, a methanol ligand has replaced the μ_2 -sulfato group of the former. Due to the non-linearity of the Fe-O-Me moiety, the methyl group is fourfold disordered (as is the μ_2 -sulfate in **1a**). The same holds for the Fe-N-O moiety, which is slightly bent with an angle of $163.3(1)^{\circ}$ with all other values similar to **1a** (Figure 2) as well: Fe-N 1.771(12) Å, N-O 1.153(18) Å, Fe-O_{sulfate} 2.059(6) Å, and Fe-O_{MeOH} 2.157(11) Å.

Among the three compounds of this work, **1b** was the most stable in terms of a lack of cleaving off nitric oxide. Thus, various spectroscopic data were collected. The N–O stretching frequency of 1837 cm⁻¹ was as high as those of the related Fe(NO)O₅ compounds, which all mark the upper limit of the quartet-{FeNO}⁷ class (for a compilation, see reference^[6]). Maxima of the Kubelka–Munk-transformed diffuse reflexion spectrum of the solid were found in the visible range at 473 and 590 nm, rather close to the respective maxima of the parent brown-ring chromophore (464 and 592 nm). The red vs. brown color has its origin in an additional absorption of the [Fe(H₂O)₅(NO)]²⁺ species in the red region close to 740 nm, which is missing for the red **1b**.

Another close resemblance was found for the zero-field ⁵⁷Fe Mößbauer data. For **1b**: isomer shift $\delta = 0.828(4) \text{ mm} \cdot \text{s}^{-1}$, quadrupole splitting: $|\Delta EQ| = 1.879(7) \text{ mm} \cdot \text{s}^{-1}$; for the ferrate of the brown-ring cation in reference^[3a,3b]: $\delta = 0.655(3) \text{ mm} \cdot \text{s}^{-1}$, $|\Delta EQ| = 2.031(8) \text{ mm} \cdot \text{s}^{-1}$.

$[\{Fe(H_2O)(NO)(\mu_2 - ox)\}_{n/n} \cdot H_2O] (2)$

On attempts to isolate further quartet-{FeNO}⁷ compounds with simple weak-field anions, the structural motif of the anion as a bridging ligand in a coordination polymer was also found with oxalate. Crystals of [{Fe(H₂O)(NO)(μ_2 -ox)}_{n/n}·H₂O] (2) were obtained in a heterogeneous reaction. In the first step, the addition of an equimolar amount of oxalic acid to an aqueous solution of ferrous triflate resulted in the precipitation of the sparingly soluble ferrous oxalate. In the second step, gaseous nitric oxide was allowed to act on the yellow slurry, which progressively deepens its color to greenish brown. After a couple of days, the fine powder became interspersed with larger brownish crystals, which reached a size suitable for X-ray analysis after about three months. The result of the crystallographic analysis is shown in Figure 3. **2** is a one-dimensional coordination polymer. The Fe(NO)O₅ coordination corresponds to **1** and to the parent aqua species $[Fe(H_2O)_5(NO)]^{2+}$. With the latter, compound **2** shares a rather limited stability in terms of rapid decomposition outside an NO atmosphere. Not surprisingly, the bonds' metrics are again similar.

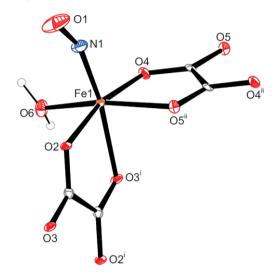


Figure 3. The coordination sphere about the Fe(NO) moiety in the brownish crystals of **2** (50% probability ellipsoids). In the polymeric strands, the next-neighboring iron atoms are chelated by the O2ⁱ/O3 and the O4ⁱ/O5 sites. Distances in Å and angles in degrees: Fe1 to: N1 1.784(6), O2 2.083(5), O3 2.166(4), O4 2.084(5), O5 2.108(4), O6 2.035(5); N1–O1 1.135(8); Fe1–N1–O1 155.6(6). Symmetry code: ⁱ –*x*, 2 – *y*, 1 – *z*; ⁱⁱ 1 – *x*, 2 – *y*, –*z*.

While the quality of the highly symmetrical (crystal class 4/mmn) red crystals of **1** is low due to pronounced disorder, the related one-dimensional polymer in the triclinic crystals of **2** can be described with more detail. As a result, the typical bent of the Fe–N–O moiety appears as a common structural feature – most developed in **2**. An interpretation in terms of orbital interactions is given in reference^[3a,3b]. As observed for all quartet-{FeNO}⁷ compounds, hydrogen-bond donors such as water molecules interact with the oxygen atoms of the anion – not with the nitrosyl ligand. A packing diagram is shown in the Supporting Information.

Conclusions

We have presented quartet-{FeNO}⁷ compounds that share an Fe(NO)O₅ coordination pattern – the same pattern, which is present in the parent "brown-ring" chromophore $[Fe(H_2O)_5(NO)]^{2+}$. Unlike this prototypic species, the new compounds are coordination polymers due to their coligands' ability to act in a bridging mode. However, the term "new compound" has to be used with reservations for **1a**. Cherryred crystals of the claimed composition FeSO₄•NO, isolated in the course of the same procedure as herein, were described more than a century ago by Manchot.^[1e] Fairly certainly, he had already held **1a** in his hands at that time. Moreover, since the same red color is observed in the bottom layer of the ring Journal of Inorganic and General Chemistry

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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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Keywords: Coordination chemistry; Iron; Nitrosyls; Coordination polymer; {FeNO}⁷ species

References

- a) V. Kohlschütter, M. Kutscheroff, Ber. Dtsch. Chem. Ges. 1904, 37, 3044–3052; b) W. Manchot, K. Zechentmayer, Justus Liebigs Ann. Chem. 1906, 350, 368–389; c) V. Kohlschütter, M. Kutscheroff, Ber. Dtsch. Chem. Ges. 1907, 40, 873–878; d) W. Manchot, Justus Liebigs Ann. Chem. 1910, 372, 179–186; e) W. Manchot, F. Huttner, Justus Liebigs Ann. Chem. 1910, 372, 153–178; f) V. Kohlschütter, P. Sazanoff, Ber. Dtsch. Chem. Ges. 1911, 44, 1423– 1432; g) W. Manchot, Ber. Dtsch. Chem. Ges. 1914, 47, 1601– 1614; h) W. Manchot, Ber. Dtsch. Chem. Ges. 1914, 47, 1614– 1616.
- [2] H. I. Schlesinger, A. Salathe, J. Am. Chem. Soc. 1923, 45, 1863– 1878.
- [3] a) G. Monsch, P. Klüfers, Angew. Chem. 2019, 131, 8654–8659;
 b) G. Monsch, P. Klüfers, Angew. Chem. Int. Ed. 2019, 58, 8566–8571;
 c) W. P. Griffith, J. Lewis, G. Wilkinson, J. Chem. Soc. 1958, 3993–3998.
- [4] a) A. In-Iam, M. Wolf, C. Wilfer, D. Schaniel, T. Woike, P. Klüfers, *Chem. Eur. J.* 2019, 25, 1304–1325; b) A. L. Speelman, B. Zhang, A. Silakov, K. M. Skodje, E. E. Alp, J. Zhao, M. Y. Hu, E. Kim, C. Krebs, N. Lehnert, *Inorg. Chem.* 2016, 55, 5485–5501.
- [5] D. Beck, A. Belz, A. In-Iam, P. Mayer, P. Klüfers, Z. Anorg. Allg. Chem. 2017, 643, 1191–1194.
- [6] A. Banerjee, J. Li, A. L. Speelman, C. J. White, P. L. Pawlak, W. W. Brennessel, N. Lehnert, F. A. Chavez, *Eur. J. Inorg. Chem.* 2018, 2018, 4797–4804.

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