

Article

## Crystallization and Structure Determination of *Fac*-Triammin-Aquo-Oxalato-Cobalt (III)-Nitrate Monohydrate

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External Editor: Nikolaus Korber

Received: 8 October 2014; in revised form: 17 November 2014 / Accepted: 19 November 2014 / Published: 28 November 2014

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**Abstract:** The title compound, *fac*-triammin-aquo-oxalato-cobalt(III)-nitrate monohydrate, *fac*-[Co(NH<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)]NO<sub>3</sub>·H<sub>2</sub>O (**2**), was prepared according to an original synthetic protocol published exactly 100 years ago by Alfred Werner by dissolving the indigo-blue non-electrolyte complex *mer*-triammin-chloro-oxalato-cobalt(III), *mer*-[Co(NH<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)Cl] (**1**), in boiling half-concentrated nitric acid. Contrary to the literature, it did not crystallize directly from the reaction mixture, but crystallization could be induced by saturating the solution with NaClO<sub>4</sub>. The structure of **2** has monoclinic (P2<sub>1</sub>/n) symmetry. The crystal structure displays an extensive array of N–H ··· O and O–H ··· O hydrogen bonding.

**Keywords:** Oxalato complexes; cobalt; Werner-type complexes; hydrogen bonds; crystal structure

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### 1. Introduction

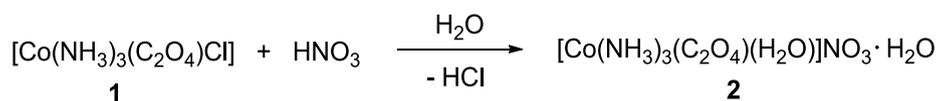
Oxalato complexes of di- and trivalent cobalt are of significant current interest because of their unusual magnetic properties [1–7] and as components of metal-organic frameworks [8,9] and 3D coordination networks [10,11]. The oxalato ligand also played a prominent role in the very beginning of

transition metal coordination chemistry. For example, the famous indigo-blue non-electrolyte complex *mer*-triammin-chloro-oxalato-cobalt (III), *mer*-[Co(NH<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)Cl] (**1**), was first reported as early as 1896 by Jørgensen [12]. Just three years earlier in 1893, Alfred Werner, the founder of modern coordination chemistry, had proposed the correct formulation of “luteocobalt chloride” as [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> [13]. Jørgensen prepared *mer*-[Co(NH<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)Cl] (**1**) by treatment of the so-called “dichrocobalt chloride” [14,15], *trans*-[Co(NH<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)Cl<sub>2</sub>]Cl, with oxalic acid in water. Due to its non-electrolyte character, the indigo-blue product [Co(NH<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)Cl] (**1**) is insoluble in water. The compound was further investigated by Alfred Werner in his comprehensive paper entitled “Über Metallverbindungen mit komplex gebundener Oxalsäure” [16] and was shown to adopt the *meridional* configuration. Werner also reported the conversion of **1** into salts containing the *fac*-[Co(NH<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)]<sup>+</sup> cation [14,16]. The nitrate of this series was first obtained by treatment of **1** with AgNO<sub>3</sub>, followed by separation of the AgCl formed during the reaction and subsequent crystallization [14]. It is also formed upon treatment of *mer*-[Co(NH<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)OH] with aqueous nitric acid (25%). A more straightforward synthetic route involves heating of a suspension of **1** in half-concentrated HNO<sub>3</sub> according to Scheme 1 until the insoluble precursor has completely dissolved. It was reported that crystallization from the reaction mixture directly affords red-purple, needle-like crystals of the title compound [16,17]. Werner correctly analyzed this salt as [Co(NH<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)]NO<sub>3</sub>·H<sub>2</sub>O (**2**) and also established the *facial* configuration of the cation, while Matsuno later incorrectly formulated the compound as *mer*-[Co(NH<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)(NO<sub>3</sub>)]·H<sub>2</sub>O [18]. We report here an X-ray structural investigation of **2** which clearly confirms Alfred Werner’s early findings.

## 2. Results and Discussion

The title compound *fac*-triammin-chloro-oxalato-cobalt (III)-nitrate monohydrate, *fac*-[Co(NH<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)]NO<sub>3</sub>·H<sub>2</sub>O (**2**), was prepared according to the original procedure reported by Werner [16]. Nitric acid was added to a blue suspension of **1** in water and the mixture was heated to boiling for a few minutes until a clear, purple solution had formed (Scheme 1).

**Scheme 1.** Preparation of the title compound *fac*-[Co(NH<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)]NO<sub>3</sub>·H<sub>2</sub>O (**2**).



According to Werner, beautiful, well-formed, red-purple crystals of **2** (“prächtig karmoisinrote Nadeln”) should form upon slight cooling of the reaction mixture. In our case, however, crystallization did not occur even on prolonged standing of the solution at 0 °C. It is well established from studies by Siebert *et al.* [19,20] that perchlorates are often particularly suitable for the isolation of various series of Werner-type cobalt(III) ammine complexes. Quite often, the perchlorates are less soluble than other salts (e.g., chlorides, bromides, nitrates) and exhibit a highly crystallinity [19,20]. Thus, we attempted to prepare the new perchlorate derivative [Co(NH<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)]ClO<sub>4</sub> by saturating the solution of **2** with solid NaClO<sub>4</sub>. Undisturbed standing of the reaction mixture at 0 °C for 2 days afforded well-formed, purple, needle-like crystals. However, an X-ray diffraction study of the product surprisingly revealed the

presence of the original nitrate *fac*-[Co(NH<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)]NO<sub>3</sub> · H<sub>2</sub>O (**2**). Obviously, the large excess of NaClO<sub>4</sub> had induced the crystallization of **2**, whereas the perchlorate salt could not be isolated.

### Crystal Structure

The title compound **2** crystallizes in the monoclinic space group P2<sub>1</sub>/n (Table 1). Figure 1 shows the molecular structure; bond lengths and angles are listed in Table 2. In the solid state, the title compound comprises a *fac*-[Co(NH<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)]<sup>+</sup> cation, an uncoordinated nitrate anion and one water molecule. Thus the X-ray study clearly confirms that a rearrangement from the *meridional* configuration in **1** to the *facial* configuration takes place during the formation of the aquo complex **2**. The average Co–N(NH<sub>3</sub>) distance in **2** is 1.936 Å. Within the chelating oxalate anion, the C–O distances to the oxygen atoms bonded to cobalt (O(1)–C(1) 1.293(5), O(2)–C(2) 1.280(5) Å) are only ca. 0.07 Å longer than the outer C–O distances (O(3)–C(1) 1.225(5), O(4)–C(2) 1.216(5) Å) which are formally C=O double bonds. The central C–C bond length in the oxalato ligand is 1.554(6) Å. As expected, these values can be favorably compared to those reported for other cobalt oxalato complexes [1–11].

**Table 1.** Crystal data and structure refinement for *fac*-[Co(NH<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)]NO<sub>3</sub> · H<sub>2</sub>O (**2**).

Identification code	ip1_167
Empirical formula	C <sub>2</sub> H <sub>13</sub> Co N <sub>4</sub> O <sub>9</sub>
Formula weight	296.09
Temperature	210(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /n
Unit cell dimensions	$a = 7.8532(16)$ Å, $\alpha = 90^\circ$ $b = 10.000(2)$ Å, $\beta = 105.06(3)^\circ$ $c = 13.192(3)$ Å, $\gamma = 90^\circ$
Volume	1000.4 (3) Å <sup>3</sup>
Z	4
Density (calculated)	1.966 Mg/m <sup>3</sup>
Absorption coefficient	1.764 mm <sup>-1</sup>
F(000)	608
Crystal size	0.40 × 0.30 × 0.07 mm <sup>3</sup>
Theta range for data collection	2.59 ° to 28.08 °
Index ranges	$-10 \leq h \leq 10$ , $-13 \leq k \leq 12$ , $-17 \leq l \leq 17$
Reflections collected	9475
Independent reflections	2403 ( $R(\text{int}) = 0.1035$ )
Completeness to theta = 28.08 °	98.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5934 and 0.4239
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	2403/33/197
Goodness-of-fit on $F^2$	0.881
Final $R$ indices ( $I > 2\sigma(I)$ )	$R1 = 0.0525$ , $wR2 = 0.1260$
$R$ indices (all data)	$R1 = 0.0793$ , $wR2 = 0.1327$
Largest diff. peak and hole	0.727 and $-0.444$ e.Å <sup>-3</sup>

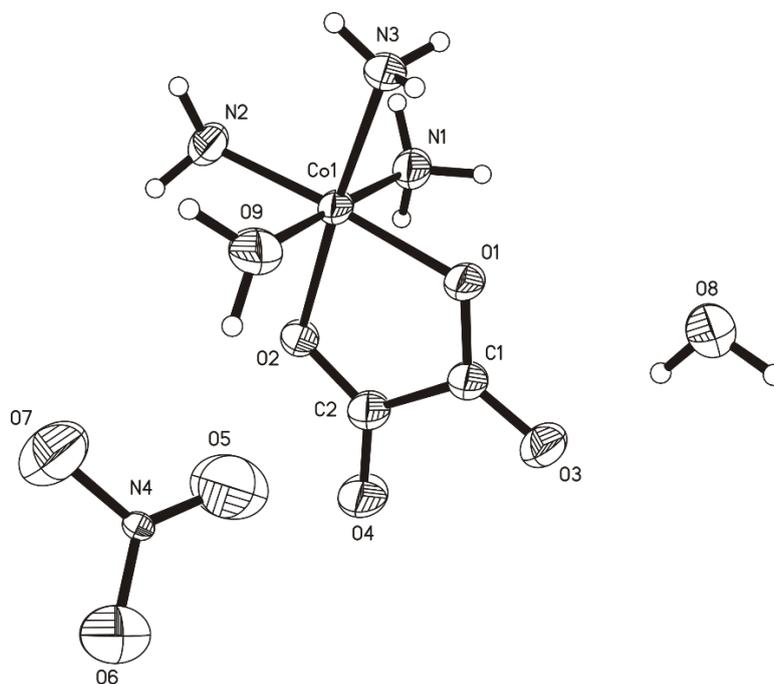
**Table 2.** Selected bond lengths (Å) and angles (°) for *fac*-[Co(NH<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)]NO<sub>3</sub> · H<sub>2</sub>O (**2**).

Co(1)–O(1)	1.915(3)	N(3)–H(3C)	0.83(3)
Co(1)–O(2)	1.915(3)	O(1)–C(1)	1.293(5)
Co(1)–N(1)	1.934(4)	O(2)–C(2)	1.280(5)
Co(1)–N(2)	1.935(4)	O(3)–C(1)	1.225(5)
Co(1)–N(3)	1.940(4)	O(4)–C(2)	1.216(5)
Co(1)–O(9)	1.943(4)	O(9)–H(9A)	0.911(17)
N(1)–H(1A)	0.91(3)	O(9)–H(9B)	0.914(17)
N(1)–H(1B)	0.92(3)	C(1)–C(2)	1.554(6)
N(1)–H(1C)	0.91(3)	O(8)–H(8A)	0.897(17)
N(2)–H(2A)	0.88(3)	O(8)–H(8B)	0.896(17)
N(2)–H(2B)	0.88(3)	N(4)–O(5)	1.197(6)
N(2)–H(2C)	0.88(3)	N(4)–O(6)	1.229(5)
N(3)–H(3A)	0.84(3)	N(4)–O(7)	1.292(5)
N(3)–H(3B)	0.84(3)	–	–
O(1)–Co(1)–O(2)	86.18(13)	Co(1)–N(2)–H(2B)	116(3)
O(1)–Co(1)–N(1)	89.80(16)	H(2A)–N(2)–H(2B)	104(6)
O(2)–Co(1)–N(1)	90.14(16)	Co(1)–N(2)–H(2C)	118(5)
O(1)–Co(1)–N(2)	176.13(15)	H(2A)–N(2)–H(2C)	98(6)
O(2)–Co(1)–N(2)	89.96(15)	H(2B)–N(2)–H(2C)	112(6)
N(1)–Co(1)–N(2)	90.45(19)	Co(1)–N(3)–H(3A)	107(4)
O(1)–Co(1)–N(3)	89.11(15)	Co(1)–N(3)–H(3B)	115(4)
O(2)–Co(1)–N(3)	175.27(16)	H(3A)–N(3)–H(3B)	101(6)
N(1)–Co(1)–N(3)	90.29(17)	Co(1)–N(3)–H(3C)	112(3)
N(2)–Co(1)–N(3)	94.75(17)	H(3A)–N(3)–H(3C)	114(5)
O(1)–Co(1)–O(9)	87.97(15)	H(3B)–N(3)–H(3C)	106(5)
O(2)–Co(1)–O(9)	90.70(15)	C(1)–O(1)–Co(1)	112.5(3)
N(1)–Co(1)–O(9)	177.56(17)	C(2)–O(2)–Co(1)	112.5(3)
N(2)–Co(1)–O(9)	91.84(19)	Co(1)–O(9)–H(9A)	113(5)
N(3)–Co(1)–O(9)	88.69(17)	Co(1)–O(9)–H(9B)	122(4)
Co(1)–N(1)–H(1A)	115(4)	H(9A)–O(9)–H(9B)	104(7)
Co(1)–N(1)–H(1B)	110(4)	O(3)–C(1)–O(1)	123.9(4)
H(1A)–N(1)–H(1B)	107(6)	O(3)–C(1)–C(2)	122.1(4)
Co(1)–N(1)–H(1C)	108(4)	O(1)–C(1)–C(2)	114.0(3)
H(1A)–N(1)–H(1C)	97(5)	O(4)–C(2)–O(2)	125.0(4)
H(1B)–N(1)–H(1C)	120(5)	O(4)–C(2)–C(1)	120.2(4)
Co(1)–N(2)–H(2A)	106(5)	O(2)–C(2)–C(1)	114.8(3)
H(8A)–O(8)–H(8B)	110(6)	O(5)–N(4)–O(7)	119.9(4)
O(5)–N(4)–O(6)	123.8(4)	O(6)–N(4)–O(7)	116.3(4)

Figure 2 shows the crystal packing of compound **2** in the solid state. The crystal structure displays an extensive network of N–H ··· O and O–H ··· O hydrogen bonding interactions (Table 3). The coordinated water molecule is connected through O–H ··· O hydrogen bonds with the water of crystallization and the uncoordinated nitrate anion. The latter also forms an N–H ··· O hydrogen bond to the NH<sub>3</sub> ligand in *trans*-position to the coordinated water in a neighboring cation. The other two, *cis*-oriented, NH<sub>3</sub> ligands in the cation form a pair of N–H ··· O hydrogen bonds with the uncoordinated oxalate oxygen atoms of

an adjacent  $[\text{Co}(\text{NH}_3)_3(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]^+$  ion. In combination, these different hydrogen bonding interactions result in a three-dimensional solid-state structure as illustrated in Figure 2.

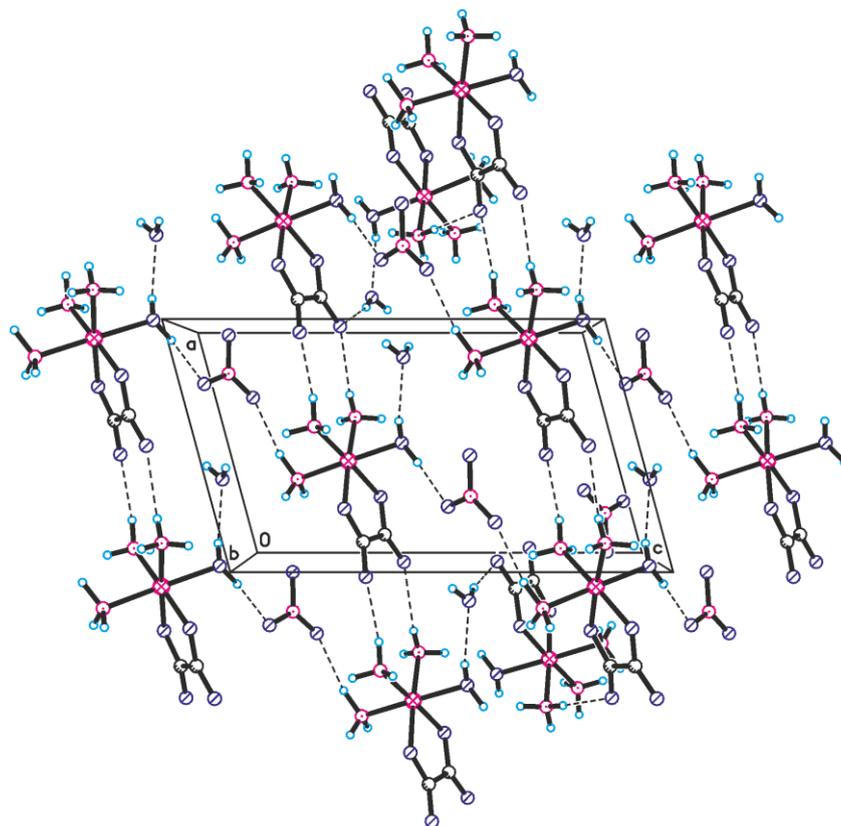
**Figure 1.** Structure of *fac*- $[\text{Co}(\text{NH}_3)_3(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]\text{NO}_3 \cdot \text{H}_2\text{O}$  (**2**) in the crystal, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.



**Table 3.** Hydrogen bond lengths (Å) and angles (°) for *fac*- $[\text{Co}(\text{NH}_3)_3(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]\text{NO}_3 \cdot \text{H}_2\text{O}$  (**2**).

D-H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(DHA)
N(1)–H(1A)··O(2)#1	0.91(3)	2.21(4)	3.076(5)	158(6)
N(1)–H(1B)··O(6)#2	0.92(3)	2.11(4)	3.017(6)	167(5)
N(1)–H(1C)··O(7)#3	0.91(3)	2.33(5)	2.976(5)	128(5)
N(1)–H(1C)··O(8)#4	0.91(3)	2.66(6)	3.091(6)	110(4)
N(2)–H(2A)··O(7)#5	0.88(3)	2.43(3)	3.304(7)	174(6)
N(2)–H(2A)··O(6)#5	0.88(3)	2.63(6)	3.239(6)	128(5)
N(2)–H(2B)··O(8)#4	0.88(3)	2.44(3)	3.273(6)	159(4)
N(2)–H(2C)··O(4)#6	0.88(3)	2.12(4)	2.956(5)	159(7)
N(3)–H(3A)··O(9)#7	0.84(3)	2.57(4)	3.348(6)	155(5)
N(3)–H(3A)··O(1)#7	0.84(3)	2.65(4)	3.361(6)	143(5)
N(3)–H(3B)··O(4)#1	0.84(3)	2.20(3)	3.035(6)	171(6)
N(3)–H(3C)··O(3)#6	0.83(3)	2.19(3)	2.963(5)	155(4)
O(9)–H(9A)··O(8)#7	0.911(17)	1.88(5)	2.690(5)	147(7)
O(9)–H(9B)··O(5)	0.914(17)	1.86(3)	2.746(6)	164(7)
O(8)–H(8A)··O(3)	0.897(17)	1.95(2)	2.844(5)	172(6)
O(8)–H(8B)··O(5)#8	0.896(17)	2.49(5)	3.185(6)	135(5)

Notes: Symmetry transformations used to generate equivalent atoms: #1:  $-x + 1/2, y - 1/2, -z + 1/2$ ; #2:  $x - 1/2, -y + 1/2, z + 1/2$ ; #3:  $x + 1/2, -y + 1/2, z + 1/2$ ; #4:  $-x + 1/2, y + 1/2, -z + 1/2$ ; #5:  $-x, -y + 1, -z$ ; #6:  $x - 1, y, z$ ; #7:  $-x, -y, -z$ ; #8:  $-x + 1, -y, -z$ .

**Figure 2.** Crystal packing of the title compound *fac*-[Co(NH<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)]NO<sub>3</sub> H<sub>2</sub>O (**2**).

### 3. Experimental Section

**Cautionary note:** Perchlorates are potentially explosive and should always be handled with great care!

The title compound, *fac*-triammin-chloro-oxalato-cobalt (III)-nitrate monohydrate, *fac*-[Co(NH<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)]NO<sub>3</sub> H<sub>2</sub>O (**2**), was prepared according to the original procedure given by Werner [16]. A 5 g-sample of indigo-blue *mer*-[Co(NH<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)Cl] (**1**) [12] was suspended in a mixture of water (30 mL) and concentrated nitric acid (20 mL). The mixture was heated to boiling until after a few minutes a clear purple solution had formed. In contrast to the original preparation, crystallization did not occur simply upon cooling of the reaction mixture to room temperature. However, crystallization could be induced by saturating the solution with solid sodium perchlorate, NaClO<sub>4</sub>. Under these conditions, purple crystals of *fac*-[Co(NH<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)]NO<sub>3</sub> H<sub>2</sub>O (**2**) were obtained after undisturbed standing at 0 °C for 2 days.

The X-ray diffraction data for compound **2** were measured at 210(2) K on a Stoe IPDS diffractometer. Structure solution and refinement were carried out using the programs SHELXS-97 [21] and SHELXL-97 [22]. The hydrogen atoms were freely refined using restraints. CCDC reference number: 1027030. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

### 4. Conclusions

Exactly 100 years after being first reported by Alfred Werner, the crystal structure of the title compound, *fac*-triammin-chloro-oxalato-cobalt(III)-nitrate monohydrate, *fac*-[Co(NH<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)]NO<sub>3</sub> H<sub>2</sub>O (**2**)

has been determined by X-ray diffraction. The crystal structure analysis confirmed both the composition and the *facial* coordination geometry of this complex which Werner had correctly proposed without the help of modern analytical techniques.

### Acknowledgments

Financial support of this work by the Otto-von-Guericke-Universität Magdeburg is gratefully acknowledged.

### Author Contributions

Frank T. Edelman carried out the experimental work (synthesis and crystallization) and prepared the manuscript. Cristian G. Hrib and Steffen Blaurock carried out the crystal structure determination.

### Conflicts of Interest

The authors declare no conflict of interest.

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