Structure of Bromotrinitrosyl Iron, [Fe(NO)₃Br], and DFT Calculations of the Structures of [Fe(NO)₃X] (X = Cl, Br, I)

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Dedicated to the Memory of Professor Reinhard Nast (1912–2004)

Abstract. Bromotrinitrosyl iron was prepared by passing a stream of nitrogen monoxide over a mixture of iron dibromide and iron powder at elevated temperatures. It readily loses NO to give $[(ON)_2Fe(\mu-Br)Fe(CO)_2]$. The structure of freshly obtained $[Fe(NO)_3Br]$ was determined by X-ray diffraction at 200 K and shows (distorted) tetrahedral coordination with N-Fe-N and N-Fe-Br angles of 107.9(2)° and 111.0(2)° and bent Fe-N-O

Introduction

Recently, the interesting history and development of the chemistry of nitrosyl iron halides was reviewed [1] and the structures of the trinitrosyl iron complexes [Fe(NO)₃Cl] [2] and [Fe(NO)₃I] [1] were determined by X-ray diffraction. In the following we report on the formation and structural characterization of [Fe(NO)₃Br]. DFT theoretical studies were carried out in order to compare the structural parameters in the series $[Fe(NO)_3X]$ (X = Cl, Br, I). The first evidence for the existence of the unstable trinitrosyl iron bromide was observed by Fischer [3] by passing nitrogen monoxide over solid, anhydrous FeBr2 and the product contained clearly more than 2 mol NO per mol Fe. The complex [Fe(NO)₃Br] was isolated from the reaction of [Fe(CO)₄Br₂] and NO as black fine needles, which sublime in an NO stream and easily lose nitrogen monoxide [4]. Similarly, the iodo and chloro complexes are formed from tetracarbonyldihalo iron [Fe(CO)₄X₂], and NO ([4] and experimental part). In this work we used a mixture of anhydrous FeBr₂ and Fe powder as starting materials for the reaction with NO. Firstly, Nast [5] succeeded in isolating chlorotrinitrosyl iron, [Fe(NO)₃Cl], by passing NO over a mixture of anhydrous FeCl₂ and Fe powder at elevated temperatures.

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groups (162.5(6)°). The DFT calculations in the series $[Fe(NO)_3X]$ (X = Cl, Br, I) reproduce well the experimental structural parameters and vibrational frequencies.

Keywords: Nitrosyl; Iron; Bromide; Halide; Crystal structure; DFT calculations

The halo bridged dimers, $[(ON)_2Fe(\mu-X)_2Fe(NO)_2]$ (X = Cl, I) with an Fe-Fe bond which often has been used for various reactions and as catalysts (see ref. [1]) have been prepared in good yields from FeX₂/Fe and NO and subsequent sublimation in vacuo [6-8].

Results and Discussion

The title complex was obtained by leading a stream of purified nitrogen monoxide over a mixture of anhydrous iron dibromide and iron powder at \sim 150 °C. Fine black needles sublimed in a slow NO stream and were immediately used for X-ray structural determination and for IR spectra.



Figure 1 Molecular structure of [Fe(NO)₃Br] in the crystal



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 $\text{FeBr}_2 + \text{Fe} + 6 \text{ NO} \rightarrow 2[\text{Fe}(\text{NO})_3\text{Br}]$

 $2[Fe(NO)_3Br] \rightarrow [(ON)_2Fe(\mu-Br)_2Fe(NO)_2] + 2 \text{ NO}$

The IR spectra (CH₂Cl₂ solution) clearly showed the two $\tilde{v}NO$ absorptions of [Fe(NO)₃Br] at 1899 cm⁻¹ (A₁) and at 1794 cm^{-1} (E). The ratio of the intensities of the two NO absorptions (1/7.9) is typical for a tetrahedral $M(NO)_3$ group [9] and an angle between the NO groups of 109 °C can be calculated from this ratio (assuming linear Fe-N-O groups [10]. Besides the vNO absorptions of [Fe(NO)₃Br] two additional NO absorptions at 1817 and 1766 cm⁻¹ appeared which can be attributed to the dimer [(ON)₂Fe- $(\mu$ -Br)₂ Fe(NO)₂ [11] which is easily formed by the loss of NO from [Fe(NO)₃Br] as was also observed by Kramolowsky [12] in the reaction of [Fe(NO)₃Br] witch PPh₃ which gives the dinitrosyl complex [Fe(NO)₂-(PPh₃)Br], OPPh₃ and N₂O. Solid [Fe(NO)₃Br] can only be stored without decomposition for some days under an atmosphere of NO.

The title complex crystallizes in the same trigonal space group P6₃mc (Table 2) as do [Fe(NO)₃Cl] [2] and [Fe(NO)₃I] [1]. The crystallographically imposed 3-fold axis makes all three Fe-N-O groups equivalent. The cell volume and the structural parameters of [Fe(NO)₃Br] lie between those of [Fe(NO)₃X] (X = Cl, I) (Table 1). The [Fe(NO)₃X] molecules (X = Cl, Br, I) show (distorted)

Table 1 Bond lengths /Å and angles /° and cell volumes /Å³ of $[Fe(NO)_3X]$

| Х | N-O | Fe-N | Fe-X | Fe-N-O | N-Fe-N | N-Fe-X | O…Fe…O | V |
|----|----------|----------|----------|----------|----------|----------|-----------|-----------|
| Cl | 1.152(5) | 1.702(4) | 2.252(2) | 161.5(4) | 106.5(2) | 112.3(2) | _ | 268.9(1) |
| Br | 1.154(7) | 1.705(5) | 2.388(2) | 162.5(6) | 107.9(2) | 111.0(2) | 99.6(2) | 288.20(3) |
| Ι | 1.145(6) | 1.706(4) | 2.588(2) | 165.5(6) | 110.3(2) | 108.6(2) | 104.6 (1) | 317.66(5) |

 Table 2
 Crystallographic Data of [Fe(NO)₃Br]

| formula | BrFeN ₃ O ₃ |
|--|--|
| formula weight | 225.77 |
| temperature / K | 200(2) |
| crystal system | hexagonal |
| space group | P6 ₃ mc |
| a /Å | 7.2950(4) |
| b /Å | 7.2950(4) |
| c /Å | 6.2533(3) |
| volume /Å ³ | 288.20(3) |
| Z | 2 |
| absorption coefficient/min ⁻¹ | 9.470 |
| density calc./Mg/m ³ | 2.602 |
| F(000) | 212 |
| range (theta)/° | 3.22 - 27.43 |
| index ranges | $-8 \le h \le 9, -9 \le k \le k, -7 \le l \le 7$ |
| reflections collected | 3097 |
| reflections unique | 265 [R(intl = 0.0927]] |
| data / restraints / parameters | 265/1/20 |
| GOOF | 1.102 |
| R_1 (all data) | 0.0319 |
| wR_2 (all data) | 0.0720 |
| $R_1 [I > 2 \sigma (I)]$ | 0.0280 |
| $wR_2 (I > 2 \sigma (I))$ | 0.0699 |
| absolute structure parameter | 0.51(3)(racemic twin refinement) |
| largest diff. peak and hole / $e \dot{A}^{-3}$ | 0.539 and -0.307 |

tetrahedral coordination (Fig.1). In the series $Cl \rightarrow Br \rightarrow I$, with increasing Fe-X bond lengths the Fe-N-O and N-Fe-N angles become larger and the N-Fe-X angles become smaller. The environment at the Fe atom in the iodo complex is closer to tetrahedral geometry. The bending of the Fe-N-O groups (Table 1) which were also found in [(ON)₂Fe(µ-I)₂Fe(NO)₂] [6] was verified by theoretical considerations [2, 13, 14].

Summerville and Hoffmann [13] noticed for nitrosyl complexes a correlation between N-M-N angles and M-N-O bending which is also observed in the [Fe(NO)₃X] series. With decreasing N-Fe-N angles an increase of Fe-N-O bending is found (Table 1). For a large series of dinitrosyl complexes a distinct linear correlation between the non bonding O···M···O angles and the N-M-N bond angles has been demonstrated [14] and this trend is observed also for [Fe(NO)₃X] (X = Br, I) (Table 1). DFT calculations by Legzdins et al. [2] on [(ON)₃FeFBF₃] confirm, that bent Fe-N-O links have an electronic origin and can be explained by MO theory.

DFT Calculations on $[Fe(NO)_3X]$ (X = Cl, Br, I)

The DFT calculations carried out in this work showed very good agreement with the experimental structural data, especially for the Fe-X bond length (Table 3). Moreover, the trends in the series $Cl \rightarrow Br \rightarrow I$ are well reproduced for

Table 3 Experimental and computational data for [Fe(NO)₃X]

| p.g. | Cl C _{3v} | Br C _{3v} | $I \\ C_{3\nu}$ |
|----------------------------------|-----------------------|-----------------------|--------------------|
| d(Fe-X) / Å | 2.252(2) | 2.388(2) | 2.588(2) |
| B3LYP/ECP ^a | 2.256 | 2.4047 | 2.615 |
| d(Fe-N) / Å | 1 702(4) | 1.705(5) | 1.70((4) |
| B3LYP/ECP ^a | 1.661 | 1.659 | 1.657 |
| d(N-O) / Å | | | |
| exptl. B3LYP/ECP ^a | 1.152(5) 1.143 | 1.154(7) 1.143 | 1.145(6) 1.143 |
| <(Fe-N-O) /° | 161 5(4) | 162 5(6) | 166 5(6) |
| B3LYP/ECP ^a | 167.6 | 170.4 | 174.5 |
| <(N-Fe-N) /° | | | |
| exptl. B3LYP/ECP ^a | 106.5(2) 111.1 | 107.9(2) 112.7 | 110.3(2) 115.0 |
| <(N-Fe-X) /° | | | |
| exptl. B3LYP/ECP ^a | 112.3(2) 107.8 | 111.0(2) 106.0 | 108.6(2) 103.1 |
| | | | |
| v(N-O), E / cm1 | | | |
| | 1789 1893 (3030) | 1794 1899 (3100) | 1798 1901(3140) |
| v (N-O), A1 / cm1 | | | |
| | 1898 1993 (398) | 1899 1993 (412) | 1895 1991 (475) |
| <i>zpe /</i> kcal mol^{-1} | 15.8 | 15.8 | 15.9 |
| $-E^{B3LYP} / a.u.$ | 974.096588 | 527.261044 | 525.300853 |

the Fe-N bond length and also for the Fe-N-O, N-Fe-N and N-Fe-X bond angles. The calculated $\tilde{v}NO$ wavenumbers are by ~100 cm⁻¹ higher than the experimental values and agree well if a linear scaling factor of 0.95 is applied.

Experimental Section

[Fe(NO)₃Br] from FeBr₂/Fe and NO [Fe(NO)₃Br] was synthesized using the apparatus described earlier [5, 15]. A slow stream of purified (using 50 % KOH solution and solid NaOH) nitrogen monoxide (Aldrich) was passed through a glass tube over a ceramic container with a mixture of ~ 2g anhydrous, sublimed FeBr₂ and excess Fe powder (Aldrich). The electric oven was heated to ~150 °C and then allowed to cool down to ~100 °C within 3 h. Black fine needles sublimed to the colder part of the tube which were collected under NO atmosphere and immediately used for X-ray structure determination and IR spectra.

IR spectra (Perkin Elmer Spectrum One, CH_2Cl_2): vNO = 1794 vs, 1899 w ([Fe(NO)₃Br]); 1766 w, 1817 w ([Fe₂(NO)₄Br₂]); 1735 w-m, cm⁻¹ (decomposition product?).

[Fe(NO)₃Br] from [Fe(CO)₄Br₂] and NO (see [4])

A slow stream of purified NO (from NaNO₂ and 50 % H₂SO₄ in a Kipp apparatus was passed over a vessel with a mixture of ~1 g [Fe(CO)₄Br₂] [16] and excess iron powder (from Fe(CO)₅) in a glass tube which was heated to 60 °C. NO is consumed. If the heating is made to quickly, sudden reaction with glowing of the solid may occur. When the consumption of NO is finished the temperature is raised to 115 °C. After 6 h bright, 1–2 cm long, black needles were sublimed to the colder part of the tube in a slow stream of NO. [Fe(NO)₃Br] (225.79) Calc.

Fe 24.74, Br 35.40, Found Fe 25.2, Br 35.6 %.

[$Fe(NO)_3Cl$] from [$Fe(CO)_4Cl_2$] and NO

As described above for $[Fe(CO)_4Br_2]/Fe$ a mixture of $[Fe(CO)_4Cl_2]$ and Fe powder treated with NO affords the complex $[Fe(NO)_3Cl]$ in an exothermic reaction.

[Fe(NO)₃Cl] (181.32) Calc.19.56, Found Cl 19.73 %.

X-ray Structure Determination of [Fe(NO)₃Br]

The data in table 2 were collected on a NONIUS KAPPA CCD with a rotating anode using Mo- K_{α} radiation. The structure was solved with direct methods by applying the program SIR 97 [17]; for the refinement the program SHELX 97 was used.

Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karslruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-606; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD 416028

Methods

All calculations were carried out using the Gaussian G03W (revision B.03) program package [18]. The structures and analytical frequencies were computed at the hybrid density functional (DFT)

B3LYP level of theory, using Becke's three parameter functional where the local and non-local correlation is provided by the LYP (the correlation functional of Lee, Yang, Parr) expression [19-21]. For N, O and Cl a polarized valence triple-zeta basis set of the type 6-311G(2df) was used.

For iron, bromine and iodine energy-consistent pseudopotentials were used [22]. The energy-consistent pseudopotentials of the Stuttgart/Cologne group are semi-local pseudopotentials adjusted to reproduce atomic valence-energy spectra. The adjustment of the pseudopotential parameters has been done in fully numerical calculations, valence basis sets have been generated a-posteriori via energy optimization. In this study we used quasirelativistic multielectron-fit Wood-Boring (MWB) pseudopotentials for bromine (ECP28MWB) [23] and iodine (ECP46MWB) [23] and a relativistic multielectron-fit Dirac-Fock (MDF) potential for iron (ECP10MDF) [24].

The bromine (7), iodine (7) and iron (16) valence electrons were treated with valence basis sets of the following contraction: Br, (14s10p2d1f)/[3s3p2d1f]; [25]; I,(14s10p3d1f)/[3s3p2d1f] [8]; Fe, (8s7p6d1f)/[6s5p3d1f] [24].

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References

- [1] W. Beck, A. Enzmann, P. Mayer, Z. Anorg. Allg. Chem. 2004, 631, 105.
- [2] T. W. Hayton, W. S. McNeil, B. O. Patrick, P. Legzdins, J. Am. Chem. Soc. 2003, 125, 12935.
- [3] Herbert Fischer, PhD thesis, 1937, Technische Hochschule München "Zur Kenntnis der Eisennitrosyl-Verbindungen" (under the supervision of W. Manchot).
- [4] W. Hieber, W. Beck, Z. Naturforsch. 1958, 13b, 194.
- [5] W. Hieber, R. Nast, Z. Anorg. Allg. Chem. 1940, 244, 23.
- [6] L. F. Dahl, E. R. de Gie, R. D. Feltham, J. Am. Chem. Soc. 1969, 91, 1653; R. H. Summerville, R. Hoffmann, J. Am. Chem. Soc. 1976, 98, 7240.
- [7] H. Soling, R. W. Asmussen, Acta Chem. Scand. 1957, 11, 1534.
- [8] B. Haymore, R. D. Feltham, *Inorg. Synth.* 1973, 14, 81; P. L. Maxfield, *Inorg Nucl. Chem. Letters* 1970, 6, 709; D. Huchette, B. Thery, F. Petit, J. Mol. Catal. 1978, 4, 433.
- [9] W. Beck, H. G. Fick, K. Lottes, K. H. Schmidtner, Z. Anorg. Allg. Chem. 1975, 416, 99.
- W. Beck, A. Melnikoff, R. Stahl, Chem. Ber. 1966, 99, 3721;
 J. G. Bullitt, F. A. Cotton, Inorg. Chim. Acta 1971, 5, 637; F. A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 5th Ed., Wiley, New York 1988, 1036.
- [11] W. Beck, K. Lottes, Chem. Ber. 1965, 98, 2672.
- [12] W. Hieber, R. Kramolowsky, Z. Anorg. Allg. Chem. 1963, 321, 94.
- [13] R. H. Summerville, R. Hoffmann, J. Am. Chem. Soc. 1976, 98, 7251.
- [14] F. L. Alkinson, H. E. Blackwell, N. C. Brown, N. C. Connelly, J. G. Crossley, A. G. Orpen, A. L. Rieger, P. W. Rieger, J. Chem. Soc., Dalton Trans. 1996, 3491 and references therein.
- [15] W. Hieber, R. Marin, Z. Anorg. Allg. Chem. 1939, 240, 247.

- [16] W. Hieber, G. Bader, *Ber. Dtsch. Chem. Ges.* 1928, *61*, 1719;
 W. P. Fehlhammer, W. A. Herrmann, K. Öfele in "Handbuch der Präparationen Anorganischen Chemie (G. Brauer ed.), Enke, Stuttgart 1981, 1956.
- [17] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidore, R. Spagna: SIR97: a new tool for crystal structure determination and refinement; *J. Appl. Crystallogr.* **1999**, *32*, 115.
- [18] Gaussian 03, Revision B.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G.

Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Oritz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.

- [19] C. Lee, W. Yang, R. G. Parr, Phys. Rev. 1988, B37, 785.
- [20] B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* 1989, 157, 200.
- [21] A. D. Becke, J. Chem. Phys. 1993, 98, 5648.
- [22] http://www.theochem.uni-stuttgart.de/pseudopotentials/ clickpse.html
- [23] Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss, *Mol. Phys.* 1993, 80, 1431.
- [24] M. Dolg, U. Wedig, H. Stoll, H. Preuss, J. Chem. Phys. 1987, 86, 866.
- [25] J. M. L. Martin, A. Sundermann, J. Chem. Phys. 2001, 114, 3408.