SHORT COMMUNICATION

NO(HSO$_4$), a Fairly Ionic Solid

Daniel Beck,[a] Anja Belz,[a] Areenan In-Iam,[a] Peter Mayer,[a] and Peter Klüfers*[a]

Dedicated to Prof. Dieter Fenske at the Occasion of his 75th Birthday

Abstract. The colourless solid NO(HSO$_4$), known as "lead-chamber crystals", was investigated ever since its first preparation more than two centuries ago. Its overall ionic nature now is confirmed by X-ray crystallography [$Pna2_1$, a = 7.3558(4), b = 6.8924(3), c = 7.7017(3) Å, Z = 4]. The next neighbours of the NO$^+$ cations are four

hydrogensulfate oxygen atoms, forming a distorted square at a distance of about 2.5 Å from the nitrogen atom. The square pattern next to the nitrogen atom is the most widespread coordination figure about an NO$^+$ ion in a nitrosyl salt. Depending on the anion, the interaction goes along with a decrease of the N–O stretch's excitation energy.

Introduction

Salts containing the NO$^+$ ion [IUPAC: oxidonitrogen(1+), CAS: nitrosyl (deprecated by IUPAC), nitrosonium] such as NO$^+$ClO$_4^-$ have been formulated for almost a century on the basis of conductivity measurements in non-hydrolysing solvents, and, since the 1930s, Raman-spectroscopic investigations which revealed the cationic nature of the nitrosyl group in terms of a valence frequency typical for an N–O triple bond. The evolving knowledge about the ionic formulation of nitrosyl salts in this era was reviewed by *Seel* in 1950.[1]

An exceptional position among the nitrosyl salts is held by the colourless solid NO(HSO$_4$) (**1**) which, as a substance of originally unknown constitution, had been prepared and investigated another century before its ionic nature was established. The reason for the early interest was the formation of **1** in the lead-chamber process which had been developed for the production of sulfuric acid which, in its final variant, followed the reaction NO$_2$ + SO$_2$ + H$_2$O → H$_2$SO$_4$ + NO. *Humphry Davy* studied this reaction systematically in the early 19th century by mixing NO$_2$ ("nitrous acid gas") and SO$_2$ ("sulphureous acid gas"). He recognised that water was required since the dry gases did not react at all.[2] When he added less water than required, according to the equation above, he observed a "beautiful white crystalline solid", which probably was NO(HSO$_4$), formed according to 3NO$_2$ + 2SO$_2$ + H$_2$O → 2NO(HSO$_4$) + NO.

The consecutive reaction of NO(HSO$_4$) with the co-product NO in H$_2$SO$_4$ solution gave rise to numerous publications on the formed "blue acid", which appears to contain the NO adduct to NO$^+$, the N$_2$O$_2^+$ radical cation.[3] The correct net for-

mula of the colourless "lead-chamber crystals" themselves, HNO$_5$S, was determined about half a century after their first preparation by *Weber* (whose formulae seem cryptic for modern readers but have been converted into current notation by his contemporary *Rammelsberg*).[4]

Though **1** has been long known, physical data have remained sparse. IR/Raman and UV/Vis data are available, the latter of which have been used to assign spectra to the NO(HSO$_4$)/H$_2$SO$_4$ aerosol collected in Venus's atmosphere by the Pioneer mission.[5] Remarkably, reliable crystal data are missing despite the fact that solid **1** is a potent nitrosating agent. It can be prepared on a laboratory scale from HNO$_3$ (> 90%) and SO$_2$(g) according to HNO$_3$ + SO$_2$ → NO(HSO$_4$).

Results and Discussion

In our group, we used to introduce the nitrosyl ligand into metal complexes by the reaction of suitable precursors with nitrosyl salts such as NO[BF$_4$] or, as an inexpensive alternative, **1**, prepared according to the latter equation. From this usage, we got to know **1** as crystalline agglomerate, which hardly permits the solid lumps to cleave to single crystals of good quality for X-ray work. We assume that others have noted the annoying properties of compound **1** as well. Hence, the lack of a reliable structure determination may be caused by a usually chatty habit of the agglomerates.

Crystal Structure

At this point, we tried to analyse a crystalline sample of **1** by means of Sheldrick's CELL NOW program, which in fact was able to break down a low-temperature set of sharp reflections into three individual sets of non-directionally intergrown single crystals. After the separation of the reflections into three sets of the same metrics, structure analysis was straightforward.

Fortunately, the analysis revealed the nitrosyl cations to be well ordered, free of a frequently observed disorder within ni-

* Prof. Dr. P. Klüfers
 E-Mail: kluef@cup.uni-muenchen.de
[a] Department Chemie der Ludwig-Maximilians-Universität München
  Butenandtstraße 5–13
  81377 München, Germany
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trosyl salts that crops up in a too short N–O distance, often less than 1 Å [see, as examples, the structure determination on the closely related salt $NO(HS_2O_7)$ with an approximately 0.8 Å N–O distance, or the disorder of the NO^+ ion in the above-mentioned perchlorate, in which the mirror plane of space group *Pnma* is perpendicular to an N–O link of 0.98 Å length].[6] In **1**, an N–O distance of 1.056 Å was found close to the values reported for other well-resolved analyses (see Tables S1 and S2, Supporting Information). Figure 1 shows the asymmetric unit and some distances. Figure 2 shows the unit cell and the metrics of the hydrogen bonds, which assemble the hydrogensulfate anions to chains along [001], the direction of projection in the figure.
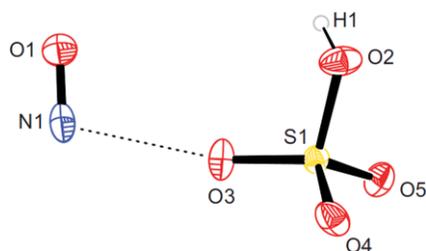

Figure 1. The asymmetric unit in crystals of **1**. The unit was chosen to contain the shortest interionic contact. Distances in Å: N1–O1 1.056(3), N1⋯O3 2.415(3); from S1 to O2 1.563(2), O3 1.447(2), O4 1.462(2), O5 1.454(2).
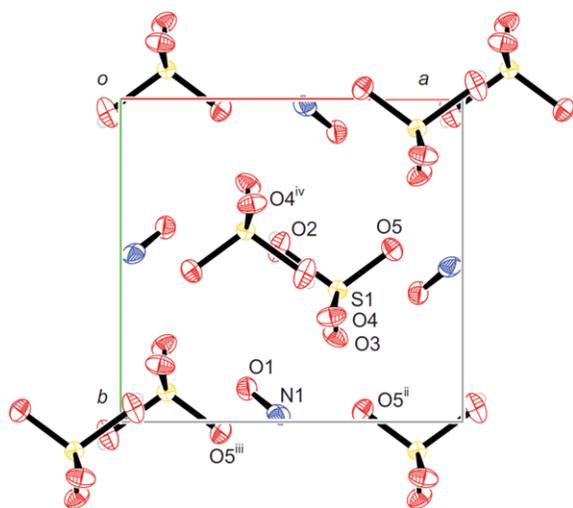
Figure 2. The unit cell of **1**, space group $Pna2_1$, projection along [001]. The atoms of the asymmetric unit are labeled without symmetry codes; O5ii and O5iii refer to Figure 3. Hydrogen-bonded HSO_4^- chains [O2–H1 0.70(5), H1⋯O4iv 1.94(5), O2⋯O4iv 2.626(3) Å; O2–H1⋯O4iv 170(5)°] are lined up along [001]; symmetry code: iv –x + 1, –y + 1, z + ½; the O4iv atom resides one unit vector length *c* below the depicted atom.

A remarkable, though by far not unique, feature of the crystal structure of **1** is highlighted in Figure 3. The nearest neighbouring atoms of the nitrogen atom stem from the non-protonated, sulfur-bonded oxygen atoms and form a distorted square with N⋯O distances of about 2.5 Å. The same motif of four N atom–anion contacts was found for the larger share of the

well-ordered structures of nitrosyl salts (Tables S1 and S2). The same holds for a first-principles-derived structure of high-pressure N_2O_4. The pattern of four N⋯O contacts is observed again, though in a markedly distorted form for this hp-$NO^+(NO_3^-)$.[7] Almost undistorted square patterns of four O atoms are found, for example, in complex nitrosyl nitratometallates such as $(NO)_2[Pd(NO_3)_4]$.[8]
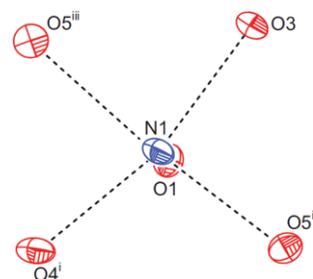
Figure 3. The cation's next neighbours. Distances in Å (σ = 0.003), from N1 to: O3 2.415, O4i 2.466, O5ii 2.472, O5iii 2.525; symmetry codes: i –x, –y, ½ + z; ii ½ – x, ½ + y, ½ + z; iii ½ + x, ½ – y, z.

DFT Calculations

Is the persistent square pattern of anion-binding sites entrenched in the electronic structure of the NO^+ building block? Figure 4a shows the electrostatic situation in terms of an ESP mapped on the van der Waals surface of the free ion (following common usage, the 0.001 a.u. surface was taken as the van der Waals shape).[9] Lone-pair regions around the poles of the N–O dumbbell are visible, leaving the surface around the N–O bond the preferred anion binding area. In a purely ionic environment, the approximate $D_{\infty h}$ symmetry of the charge distribution may contribute to the frequently encountered N/O disorder in so many crystal structures.
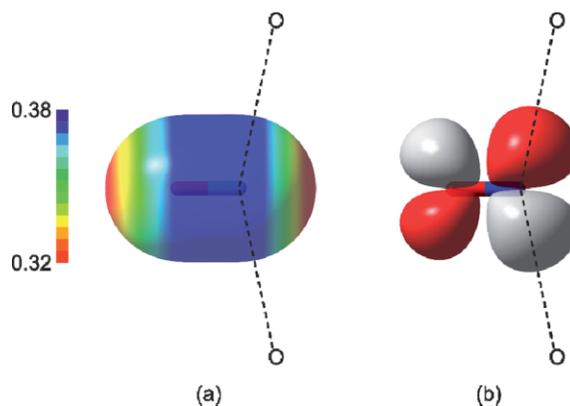

Figure 4. (a) The electrostatic potential (ESP) of the NO^+ ion (O left, N right; atomic units), mapped on the 0.001 a.u. (ca. 0.0067 e Å^{-3}) surface of the total electron density. (b) One of the two degenerate LUMOs, the N–O-π* orbitals (isovalue 0.05). For both (a) and (b), two oxygen atoms are drawn at the mean distance and the mean O≡N⋯O angle of the crystal structure of **1**. All values for (a) and (b) were taken from a BP86/def2-TZVP calculation on the free NO^+ ion with Gaussian 09.

The pattern of four N-bonded neighbours in the well-ordered structures, however, points to an orbital contribution to the bonds' overall ionic character. Figure 4b shows, for the plane of one of the two degenerate N–O-π^* LUMOs, the match of the orbital lobes on the N atom and the direction of the donor oxygen atoms of the adjacent sulfate anions in the crystal structure of **1**. To that end, it is not the electrostatic surface alone that determines the anion-binding sites of the nitrosyl cation, but the interaction between filled anion orbitals and the two degenerate LUMOs of the cations supplements the electrostatic attraction. Simple nitrosyl salts thus show a contribution to their bonding that is, to a much more pronounced extent, classified as charge-transfer adduct formation as in the NO+/disulfide couple.[10]

Though the structure analyses on well-ordered nitrosyl salts such as **1** did not reveal disorder, the experimentally determined N–O distances do not mirror the interaction – possibly since the usual fit of the electron density in terms of thermal ellipsoids is a too rough approximation to the density distribution of a triply bonded diatomic unit. As a more reliable probe, vibrational spectroscopy seems to reflect this contribution to bonding.[11] Concomitantly, the range for a nitrosyl salt N–O stretch varies with the anion, with the exception of a pretty narrow range for the entire class of weakly coordinating anions X$^-$ in salts NO+X$^-$: [B(CF$_3$)$_4$]$^-$ 2337 cm^{-1}, [BF$_4$]$^-$ 2340 cm^{-1}, [PF$_6$]$^-$ 2339 cm^{-1}, [AsF$_6$]$^-$ 2339 cm^{-1}, and [SbF$_6$]$^-$ 2342 cm^{-1}.[11b,12] On the BP86/def2-TZVP level of theory, a well-matching value of 2358 cm^{-1} is obtained for the free NO+ ion [d(N–O) = 1.070 Å]. Note that no X-ray data are available for any of these salts.

Tables S1 and S2 (Supporting Information) present the available reliable X-ray analyses on nitrosyl salts. Table S1 additionally contains data from vibrational spectroscopy. Two points are notable: (1) the pattern-of-four is the typical structural motif of a nitrosyl salt. (2) Lower ν(NO) values such as the Raman frequency of 2275 cm^{-1} for **1** are found for the better nucleophiles, as are the hydrogensulfate ion, the noncoordinating nitrate ion, or a chlorine-based anion in Table S1.

The decrease in the energy of the N–O stretch as a result of the N–O-π^* population by the anion may be illustrated by investigating an NO+HSO$_4^-$ ion pair in a computational approach. In fact, two minimum structures were found on the BP86/def2-TZVP level of theory (Figure 5).

(*syn, E* = 1.7 kJ mol^{-1})   (*anti, E* = 0)
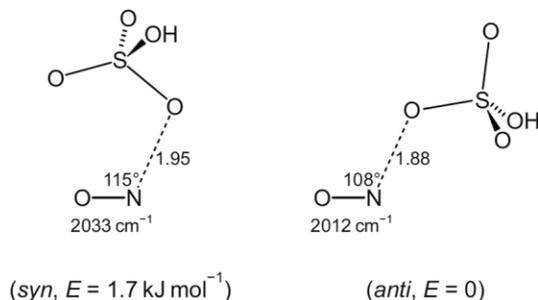
Figure 5. The two minima of about equal stability on the conformational hypersurface of an NO(HSO$_4$) entity on the BP86/def2-TZVP level of theory (N···O distances in Å), and the corresponding N–O stretches; compare: ν(NO) = 2358 cm^{-1} for the free NO+ ion calculated on the same level.

The overall ionic nature of the macroscopic crystal is mirrored in the ion pair in terms of the rather long distances from the N-atom to its neighbouring hydrogensulfate oxygen atom. At the same time, the N–O stretch is excited at lower frequencies which, however, still are clearly higher than compounds with a higher weight of the covalent O=N–X formula such as the fluoride ONF with ν(NO)$_{calc}$ = 1868 cm^{-1} on the same level of theory (for the fluoride, an experimental value of 1843 cm^{-1} is available as another check for the adequacy of the chosen BP86/def2-TZVP level[13]).

Conclusions

We have presented the crystal structure of one of the oldest reactive intermediates and synthetic building blocks of inorganic chemistry, the "lead-chamber crystals", NO(HSO$_4$). Despite the fact that the structure belongs to the overall ionic type, the cation shows a pattern of four anion-binding sites close to its N terminus. An adequate description of contributions to bonding that modify a purely electrostatic interaction in terms of bonding directions or IR/Raman-frequency shifts ("charge transfer", "polarization", "covalency") currently is a point of controversy.[14] Notably, the pattern-of-four appears to be a general feature of nitrosyl salts. It is observed in the structures of the majority of the well-ordered members of this class, but is either not present or obscured by disorder in the remaining analyses.

Experimental Section

Preparation of 1: Crystals of NO(HSO$_4$) (**1**) were prepared as intertwined agglomerates following a modified published procedure.[15] Nitric acid (ca. 90 %, 30 mL) and glacial acetic acid (11 mL) were mixed in a nitrogen atmosphere and cooled to –5 °C. A moderate stream of SO$_2$ was passed through the acid mixture. As a crucial point, the temperature of the exothermic reaction has to be kept between –5 and +5 °C! Excess SO$_2$ was absorbed in diluted KOH. After 3 h, a crystalline paste had formed. Air- and moisture-sensitive, colourless crystals of **1** were isolated by filtration, washed with cooled glacial acetic acid and dichloromethane, and dried in vacuo (36.5 g, 0.29 mol, ca. 40 % with reference to nitric acid).

Crystallographic Data: HNO$_5$S, M_r = 127.08 g mol^{-1}, colourless platelet, $0.100 \times 0.080 \times 0.020$ mm, orthorhombic, space group *Pna*2$_1$, a = 7.3558(4), b = 6.8924(3), c = 7.7017(3) Å, V = 390.47(3) Å^3, Z = 4, ρ = 2.162 g cm^{-3}, T = 100(2) K, μ(Mo-K_α) = 0.732 mm^{-1}, multi-scan absorption correction with TWINABS [Bruker AXS Inc., Madison, Wisconsin, USA, 2001], data collected with a Bruker D8 Venture TXS diffractometer equipped with a multilayer focusing mirror (Mo-K_α radiation, λ = 0.71073Å), θ range: 3.97°–27.15°, 4760 reflections collected, 468 independent and used in refinement, 452 with $I \geq 2\sigma(I)$, R_{int} = 0.0363, mean $\sigma(I)/I$ = 0.0203; a list of 1098 reflections has been used to determine three randomly distributed components of identical unit cell by means of G. Sheldrick's CELL NOW [Version 2008/4, Göttingen, Germany, 2008], the volume fractions of the three components refined to 0.84, 0.11, and 0.05; 70 parameters, $R(F_{obs})$ = 0.0243, $R_w(F^2)$ = 0.0715, S = 1.270, Flack parameter: –0.2/(14), min. and max. residual electron density: –0.314 and 0.259 e Å^{-3}, max. shift/error: 0.001, programs used: SHELXT, VERSION 2014/5, for structure solution, SHELXL-2014 for structure refinement.[16]

Crystallographic data (excluding structure factors) for the structure 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 number CCDC-1563760 (Fax: +44-1223-336-033; E-Mail: deposit@-ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Lindström **and** ***Löscher's*** **Powder Diffractogram:** An X-ray powder diagram of **1** was reported half a century ago and was indexed with an orthorhombic unit cell [a = 10.682(4), b = 11.648(8), c = 10.367(7)].[17] Though the assigned cell is different from our data, the tabulated diffraction pattern resembles the pattern calculated from our single-crystal data in a LAZY PULVERIX run.[18]

DFT Calculations: Computations were performed with Orca 3 at the BP86/def2-TZVP level of theory. For the ion pairs in Figure 5, CO-SMO(water) was included as an approach to the high-permittivity situation in an ionic environment, as well as Grimme's van der Waals correction.[19] The calculations on free NO^+ and ONF were done with Gaussian 09 at the BP86/def2-TZVP level taking the def2 basis from the Turbomole basis set library II (http://cosmologic-services.de/basis-sets/basissets.php); Figure 4 was drawn with GaussView 5 (the Gaussian reference is included in the Supporting Information).

Supporting Information (see footnote on the first page of this article): Tables S1 and S2 in the SI present the available reliable X-ray analyses on nitrosyl salts. Table S1 additionally contains data from vibrational spectroscopy.

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