

Structure and FTIR spectra of 3 : 2 complexes of trimethylamine *N*-oxide and 4-dimethylamine-2,6-dimethylpyridine *N*-oxide with perchloric acid

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Received 19 June 1995; accepted in final form 14 August 1995

Abstract

Trimethylamine *N*-oxide and 4-dimethylamine-2,6-dimethylpyridine *N*-oxide form three types of crystalline complexes with perchloric acid, with the base-to-acid ratio 1 : 1, 2 : 1 and 3 : 2, which are easily distinguished by their IR absorption. The asymmetric unit of the P1 unit cell contains two $(\text{Me}_3\text{NO})_3 \cdot (\text{HClO}_4)_2$ formula units. Each of the formula units assembles into a $(\text{Me}_3\text{NO})_3 2\text{H}^+$ dication and two independent ClO_4^- anions which show no H-bond interactions with the cationic components. The oxygen atom of a central trimethylamine *N*-oxide molecule accepts hydrogen bonds from two protonated trimethylamine *N*-oxide cations with $\text{O} \cdots \text{O}$ distances in the range 2.537(5) – 2.562(7) Å. The $\text{O} \cdots \text{H} - \text{O}$ bonds are linear and formed along direction of the two electron lone-pairs on the oxygen atom. In acetonitrile solutions the 3 : 2 complexes exist as mixtures of the 1 : 1 and 2 : 1 complexes.

1. Introduction

Heterocyclic *N*-oxides have been shown to form with strong mineral acids stable 1 : 1 and 2 : 1 complexes, with different H-bonds [1]. In crystals, the 2 : 1 complexes consist of two crystallographically equivalent *N*-oxide residues, joined by a short H-bond ($\text{O} \cdots \text{O}$ distance 2.40 ± 0.05 Å) [2,3]. In addition to the 1 : 1 and 2 : 1 complexes, trimethylamine *N*-oxide and 4-dimethylamine-2,6-dimethylpyridine *N*-oxide when reacted with HClO_4 or HBF_4 ,

also form 3 : 2 complexes. So far, the hydrogen bonding pattern in the 3 : 2 complexes has been unknown. We have undertaken the present crystal structure determination of the $(\text{Me}_3\text{NO})_3 \cdot (\text{HClO}_4)_2$ complex [4] to address this problem.

2. Experimental

Crystalline 1 : 1, 2 : 1 and 3 : 2 complexes of trimethylamine *N*-oxide have been prepared according to previously published methods [4].

4-NMe₂-2,6-Me₂C₅H₂NO · HClO₄ was prepared

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Table 1
Summary of data collection

Crystal-to-plate distance (mm)	69.5	69.7	130	161.5	230
Resolution limits (Å)	5–0.8	3–0.81	10–1.2	5–1.3	20–2.0
Oscillation per image (deg)	2.0	2.0	3.5	4.0	6.0
Number of images	94	98	52	45	35

by mixing equivalents (0.02 mol) of aqueous (ca. 70%) perchloric acid with *N*-oxide in about 5 cm³ of methanol. The solvent was evaporated and the residue dried over P₂O₅ and recrystallized from methanol–chloroform (1:3), m.p. 205°C. Calculated for C₉H₁₅ClN₂O₅: C, 40.53; H, 5.66; N, 10.50%; found: C, 40.47; H, 5.61; N, 10.52%.

(4-NMe₂-2,6-Me₂C₅H₂NO)₂·HClO₄ crystallized when 0.03 mol of *N*-oxide in 5 cm³ of ethanol was mixed with 0.02 mol of aqueous (ca. 70%) perchloric acid, m.p. 225°C. Calculated for C₁₈H₂₉ClN₄O₆: C, 49.94; H, 6.75; N, 12.94%; found C, 50.01; H, 6.74; N, 13.02%.

(4-NMe₂-2,6-Me₂C₅H₂NO)₃·(HClO₄)₂ was prepared by adding 0.01 mol of aqueous (ca. 70%) perchloric acid to 0.025 mol of *N*-oxide in 9 cm³ ethanol. After about 24 h the crystals were filtered off, washed with ethanol and dried over P₂O₅, m.p. 198°C. Calculated for C₂₇H₄₄Cl₂N₆O₁₁: C, 46.35; H,

6.34; N, 12.01%; found: C, 46.58; H, 6.46; N, 12.40%.

Colorless crystals of (Me₃NO)₃·(HClO₄)₂ were grown by slow, multiple evaporation of an ethanol solution in a refrigerator. A needle-like single crystal (0.3 × 0.3 × 0.8 mm) was mounted on a glass fiber. Intensity data were collected with Mo *K*α radiation using a Mar Research 180 mm image plate scanner mounted on a Siemens rotating anode generator. The beam was attenuated for the low-resolution data set. Five diffraction data sets were collected on the same crystal at room temperature. The data-collection parameters are summarized in Table 1. The images were processed using the DENZO SCALEPACK package [5]. The total number of independent reflections measured was 7725, making up 95.7% of the unique data to 0.81 Å. The overall merging *R* factor for all five data sets was 4.5%, with a value of 9.8% for the

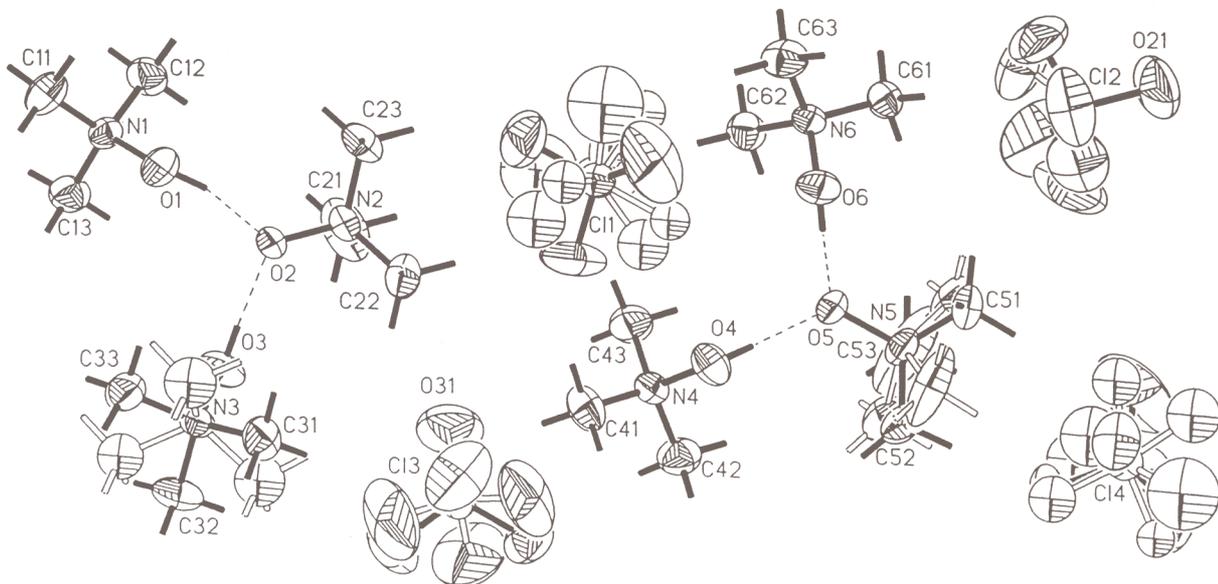


Fig. 1. Atom labelling. The two (Me₃NO)₃(HClO₄)₂ formula units are shown with atom labels. The perchlorate anions and the protonated (N3) and unprotonated (N5) *N*-oxides are disordered. The ellipsoids have been drawn at 50% probability level.

Table 2

Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for $(\text{Me}_3\text{NO})_3(\text{HClO}_4)_2$. U_{eq} is defined as one third of the trace of the orthogonalized U_{eq} tensor

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
N(1)	5599(5)	1565(1)	267(1)	43(1)
O(1)	7007(4)	1879(2)	847(1)	55(1)
C(11)	7295(8)	1287(3)	-198(2)	70(1)
C(12)	4005(8)	944(2)	488(2)	64(1)
C(13)	4271(8)	2137(2)	-59(2)	63(1)
N(2)	3647(5)	2150(2)	2333(1)	46(1)
O(2)	4677(5)	2432(1)	1757(1)	54(1)
C(21)	1075(9)	2137(4)	2208(3)	102(2)
C(22)	4509(12)	2626(3)	2936(2)	88(2)
C(23)	4324(10)	1388(2)	2442(3)	77(1)
N(3)	4960(5)	4213(1)	1301(1)	44(1)
O(3)	3196(5)	3638(1)	1367(2)	64(1)
C(31)	6409(10)	4347(3)	1954(2)	68(2)
C(32)	3619(10)	4865(2)	1128(3)	70(2)
C(33)	6345(10)	4025(3)	729(3)	70(2)
C(31')	7266(16)	3911(11)	1327(29)	103(16)
C(32')	5090(79)	4713(20)	1907(16)	103(16)
C(33')	4504(51)	4588(17)	648(11)	83(12)
N(4)	5233(5)	3491(2)	5252(2)	46(1)
O(4)	6638(5)	3254(2)	5821(2)	63(1)
C(41)	6958(8)	3793(3)	4777(2)	71(1)
C(42)	3795(8)	4073(2)	5482(2)	67(1)
C(43)	3742(9)	2858(2)	4928(2)	72(1)
N(5)	3575(5)	2828(2)	7292(2)	56(1)
O(5)	4307(5)	2536(1)	6682(1)	60(1)
C(51)	4621(19)	2421(5)	7883(3)	95(4)
C(52)	4631(20)	3590(3)	7419(5)	77(3)
C(53)	1029(9)	2784(14)	7198(8)	180(13)
C(51')	2325(62)	3494(13)	7137(8)	147(16)
C(52')	5547(25)	3238(19)	7685(11)	143(16)
C(53')	1947(39)	2287(8)	7599(9)	94(8)
N(6)	5666(5)	809(1)	6376(1)	41(1)
O(6)	6943(5)	1482(1)	6591(2)	60(1)
C(61)	4355(8)	513(2)	6945(2)	59(1)
C(62)	4082(8)	930(2)	5765(2)	60(1)
C(63)	7450(8)	303(2)	6206(3)	67(1)
Cl(1)	-1039(2)	1386(1)	4227(1)	54(1)
O(11)	-3454(11)	1106(6)	4246(5)	152(5)
O(12)	282(18)	1201(7)	4768(4)	193(6)
O(13)	-1041(15)	2154(3)	4095(5)	126(3)
O(14)	-413(17)	1077(5)	3576(3)	135(3)
O(11A)	-779(25)	1709(8)	4930(5)	61(3)
O(12A)	-195(43)	678(8)	4277(13)	239(23)
O(13A)	-3519(16)	1293(11)	4072(9)	72(5)
O(14A)	90(34)	1841(11)	3792(8)	129(8)
O(11B)	1408(16)	1502(8)	4068(8)	73(4)
O(12B)	-1056(27)	688(6)	4582(8)	75(4)
O(13B)	-2476(33)	1301(13)	3631(8)	225(19)
O(14B)	-1512(31)	1942(8)	4678(9)	103(6)
Cl(2)	824(2)	310(1)	8477(1)	53(1)

Table 2 continued

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
O(21)	116(10)	29(3)	9091(2)	147(2)
O(22)	2633(26)	872(7)	8606(6)	160(8)
O(23)	-1036(23)	574(11)	8094(6)	274(13)
O(24)	1708(28)	-272(5)	8095(6)	139(6)
O(22A)	49(31)	-74(10)	7886(4)	154(9)
O(23A)	121(38)	1055(6)	8430(10)	191(12)
O(24A)	3346(12)	385(12)	8529(6)	136(8)
Cl(3)	849(2)	4581(1)	3426(1)	59(1)
O(31)	-364(11)	3899(2)	3226(3)	151(2)
O(32)	255(17)	4889(4)	4044(4)	106(4)
O(33)	779(21)	5089(4)	2903(4)	129(5)
O(34)	3308(11)	4438(6)	3541(6)	149(6)
O(32A)	1957(30)	4552(8)	4075(5)	176(12)
O(33A)	-1090(20)	5049(6)	3470(10)	178(9)
O(34A)	2257(28)	4876(8)	2948(7)	216(12)
Cl(4)	281(2)	3627(1)	9178(1)	55(1)
O(41)	2757(10)	3509(5)	9217(5)	95(3)
O(42)	-150(16)	3953(5)	8507(3)	81(2)
O(43)	-215(22)	4088(6)	9697(4)	157(6)
O(44)	-967(23)	2932(5)	9133(7)	229(10)
O(41A)	2522(21)	3479(11)	8974(10)	142(13)
O(42A)	-1412(27)	3602(10)	8653(7)	127(7)
O(43A)	577(21)	4333(5)	9540(6)	56(3)
O(44A)	-293(31)	3110(7)	9708(7)	116(6)
O(41B)	-2243(14)	3599(7)	9238(7)	82(4)
O(42B)	726(26)	2884(5)	9053(7)	89(4)
O(43B)	798(27)	4056(8)	8608(6)	85(6)
O(44B)	1433(32)	3908(11)	9786(7)	209(15)

highest resolution shell. The relatively large R is justified by the disorder affecting the perchlorate anions and two N -oxide units.

The crystal data for $(\text{Me}_3\text{NO})_3 \cdot (\text{HClO}_4)_2$ are as follows: triclinic, space group $\text{P}\bar{1}$, $a = 5.77(3)$, $b = 18.24(3)$, $c = 19.64(3)$ \AA , $\alpha = 91.0(1)$, $\beta = 94.2(1)$, $\gamma = 94.8(1)^\circ$, $V = 2054(12)$ \AA^3 , $Z = 4$, $D_x = 1.3798$ g cm^{-3} , $\mu(\text{Mo}, K\alpha) = 0.37$ mm^{-1} , $T = 292$ K.

The structure was solved by direct methods using the program SHELXS-86 [6] and refined by the full-matrix least-squares method on F^2 with SHELXL-93 [7]. During the refinement process it became evident that two of the trimethylamine N -oxide units and all four perchlorate anions are disordered. Constraints were imposed on intramolecular distances in the disordered ions. The N -oxide units 3 and 5 and anions 2 and 3 (for labels see Fig. 1) have been found in two orientations related to each other by 60° rotation about the $\text{N}-\text{O}$ or one

Table 3
Geometry of hydrogen bonds in $(\text{Me}_3\text{NO})_3 \cdot (\text{HClO}_4)_2$

D–H...A	D...A (Å)	D–H (Å)	H...A (Å)	D–H...A (deg)
O(1)–H(1O)···O(2)	2.558(6)	0.99	1.59	164
O(3)–H(3O)···O(2)	2.537(5)	0.91	1.64	167
O(4)–H(4O)···O(5)	2.549(6)	0.94	1.62	166
O(6)–H(6O)···O(5)	2.562(7)	1.01	1.57	167

of the Cl–O bonds, respectively. For anions 1 and 4 three different orientations could be indicated. Occupancy of the less populated orientations (primed ones) are 0.13(1), 0.34(1) for *N*-oxides 3, 5, and 0.44(2), 0.43(2) for perchlorates 2, 3, respectively. For perchlorate 1, the principal orientation has an occupancy of 0.6 while the occupancies of the remaining two orientations have been set at 0.2 each. For perchlorate 4 those values are 0.5 and

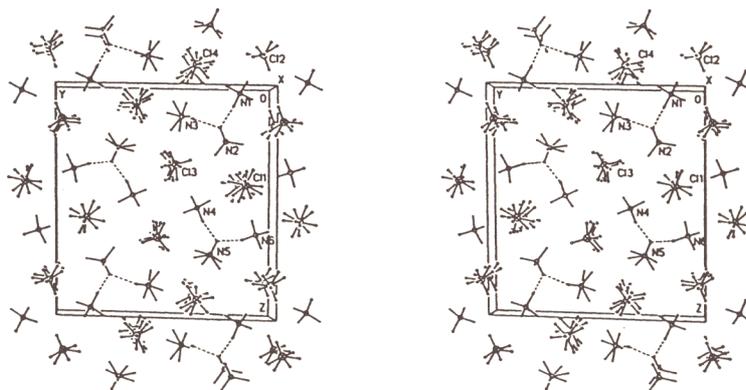


Fig. 2. Stereoview showing packing of the cationic and anionic units in the crystal.

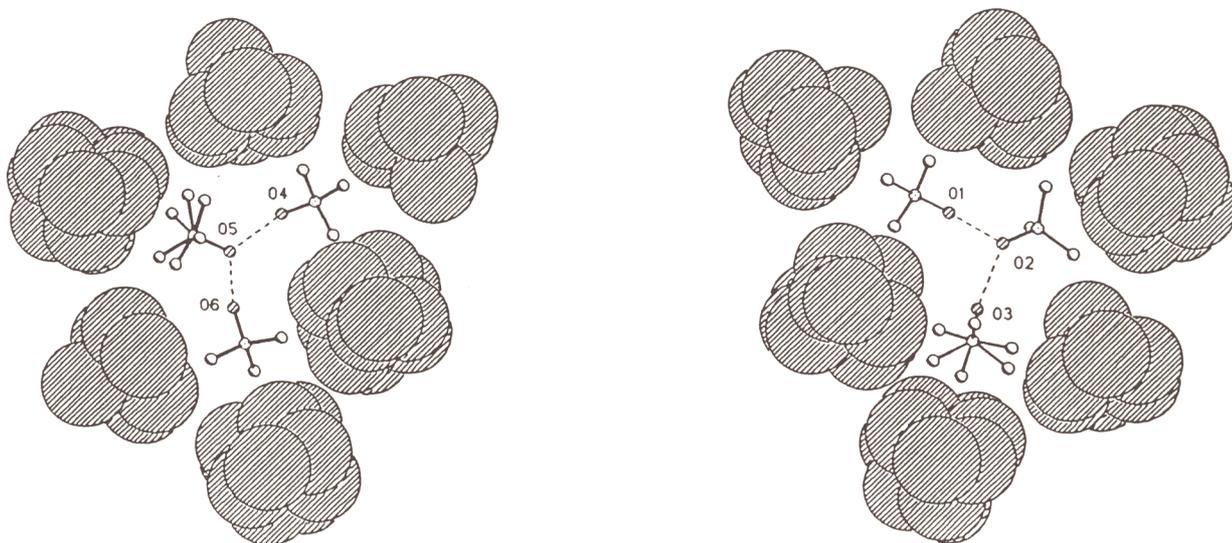


Fig. 3. Packing of the ClO_4^- anions around the $(\text{Me}_3\text{NO})_3 \cdot 2\text{H}^+$ cations.

Table 4
Bond lengths and bond angles for $(\text{Me}_3\text{NO})_3(\text{HClO})_4)_2$

Bond	Distance (Å)	Bond	Distance (Å)
N(1)–O(1)	1.430(4)	N(4)–O(4)	1.428(5)
N(1)–C(11)	1.499(6)	N(4)–C(41)	1.492(6)
N(1)–C(12)	1.489(6)	N(4)–C(42)	1.485(6)
N(1)–C(13)	1.473(5)	N(4)–C(43)	1.484(6)
N(2)–O(2)	1.401(4)	N(5)–O(5)	1.409(4)
N(2)–C(21)	1.485(10)	N(5)–C(51)	1.506(5)
N(2)–C(22)	1.487(6)	N(5)–C(52)	1.479(5)
N(2)–C(23)	1.490(6)	N(5)–C(53)	1.463(9)
N(3)–O(3)	1.413(5)	N(6)–O(6)	1.418(4)
N(3)–C(31)	1.485(6)	N(6)–C(61)	1.480(5)
N(3)–C(32)	1.503(6)	N(6)–C(62)	1.485(6)
N(3)–C(33)	1.477(6)	N(6)–C(63)	1.490(6)
N(3)–C(31')	1.481(9)	N(5)–C(51')	1.489(6)
N(3)–C(32')	1.480(6)	N(5)–C(52')	1.469(7)
N(3)–C(33')	1.480(6)	N(5)–C(53')	1.473(6)
Bond angles	Value (°)	Bond angles	Value (°)
O(1)–N(1)–C(11)	105.0(4)	O(4)–N(4)–C(41)	104.1(4)
O(1)–N(1)–C(12)	109.6(3)	O(4)–N(4)–C(42)	109.4(3)
O(1)–N(1)–C(13)	109.4(3)	O(4)–N(4)–C(43)	110.3(3)
C(13)–N(1)–C(12)	111.0(4)	C(43)–N(4)–C(42)	111.0(4)
C(13)–N(1)–C(11)	111.4(4)	C(43)–N(4)–C(41)	110.9(4)
C(12)–N(1)–C(11)	110.3(4)	C(42)–N(4)–C(41)	110.9(4)
O(2)–N(2)–C(21)	108.6(4)	O(5)–N(5)–C(51)	108.6(4)
O(2)–N(2)–C(22)	108.6(3)	O(5)–N(5)–C(52)	110.4(4)
O(2)–N(2)–C(23)	109.0(3)	O(5)–N(5)–C(53)	105.3(5)
C(21)–N(2)–C(22)	111.2(5)	C(51)–N(5)–C(52)	102.8(6)
C(21)–N(2)–C(23)	109.7(4)	C(51)–N(5)–C(53)	116.9(11)
C(22)–N(2)–C(23)	109.7(4)	C(52)–N(5)–C(53)	112.8(11)
O(3)–N(3)–C(31)	110.5(3)	O(6)–N(6)–C(61)	109.3(3)
O(3)–N(3)–C(32)	103.5(4)	O(6)–N(6)–C(62)	109.8(3)
O(3)–N(3)–C(33)	108.7(4)	O(6)–N(6)–C(63)	105.5(4)
C(33)–N(3)–C(31)	112.6(5)	C(63)–N(6)–C(61)	110.0(3)
C(33)–N(3)–C(32)	110.3(4)	C(63)–N(6)–C(62)	110.7(4)
C(31)–N(3)–C(32)	110.7(4)	C(61)–N(6)–C(62)	111.4(4)
O(3)–N(3)–C(31')	109.7(7)	O(5)–N(5)–C(51')	109.3(5)
O(3)–N(3)–C(32')	109.2(7)	O(5)–N(5)–C(52')	110.3(6)
O(3)–N(3)–C(33')	109.5(7)	O(5)–N(5)–C(53')	110.2(5)
C(33')–N(3)–C(31')	111(3)	C(53')–N(5)–C(51')	108(2)
C(33')–N(3)–C(32')	113(3)	C(53')–N(5)–C(52')	123(2)
C(32')–N(3)–C(31')	104(3)	C(52')–N(5)–C(51')	94(2)

0.25, respectively. All non-hydrogen atoms of the *N*-oxides 1, 2, 4, 6, and of the anions 2 and 3 were refined with anisotropic displacement parameters. For cation 3, *N*-oxide 5 and anions 1 and 4 only the non-hydrogen atoms of the dominating orientations were refined anisotropically. Except H(1O), H(3O), H(4O) and H(6O) (which were located

from a difference-Fourier map), the hydrogen atoms were placed in calculated positions with isotropic displacement parameters 0.02 \AA^2 higher than the U_{eq} of the atoms to which they are bonded. Positional and displacement parameters of all hydrogen atoms were not refined. The structure was refined to a final $R = 0.081$, $wR2 = 0.229$

and $S = 1.04$ for 7725 reflections and 615 parameters. The highest peak and the deepest hole in the ΔF map are 0.75 and $-0.42 \text{ e}\text{\AA}^{-3}$, respectively. Final atomic coordinates are given in Table 2. Lists of anisotropic displacement parameters, structure factors and hydrogen coordinates have been deposited with the B.L.L.D. as Supplementary Publication No. SUP26553 (5 pages). The numbering scheme of the atoms is shown in Fig. 1. Crystallographic calculations were performed in the Poznań Supercomputing and Networking Center. The FTIR spectra were measured on a Bruker IFS 113v instrument.

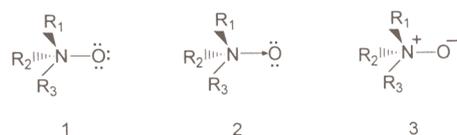
3. Results and discussion

3.1. Crystal structure

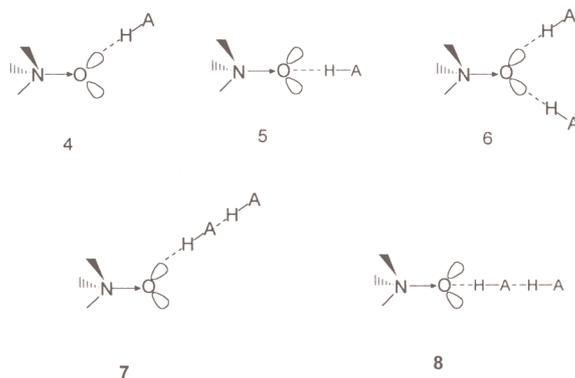
The asymmetric unit of the $P\bar{1}$ unit cell contains two $(\text{Me}_3\text{NO})_3 \cdot (\text{HClO}_4)_2$ formula units, i.e. four perchlorate anions, four protonated and two neutral *N*-oxide moieties. The trimethylamine *N*-oxide moieties assemble into two $(\text{Me}_3\text{NO})_3 \cdot 2\text{H}^+$ dications with the oxygen atom of a central trimethylamine *N*-oxide molecule accepting hydrogen bonds from two protonated trimethylamine *N*-oxide cations. The $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds are medium strong with donor–acceptor distances in the 2.537(5)–2.562(7) Å range (Table 3). Therefore, it is unlikely that the protons are centered in those hydrogen bridges. The differences in the N–O bond lengths in the peripheral *N*-oxides of both cationic units are within 3 esds (Table 4). These bonds are all longer [1.430(4), 1.413(5), 1.428(5), 1.418(4) Å] than the N–O bonds of the central units [1.401(4), 1.409(4) Å]. The N–O bond lengths found in unprotonated aliphatic tertiary amine oxides lie in the range 1.383–1.402 Å, with a mean of 1.391 Å [8]. The packing of the cationic and anionic units in this ionic crystal is shown in Fig. 2. The dicationic $(\text{Me}_3\text{NO})_3 \cdot 2\text{H}^+$ units are arranged into columns along the **a** axis and are separated from adjacent cationic columns by perchlorate anions (Fig. 3). The *x* coordinates of the N atoms are about 0.5 while those of the perchlorate Cl atoms about 0. The perchlorate anions are surrounded by 8 (anions 1 and 4) or 10 (anions 2 and

3) *N*-oxides which form highly distorted cubes or pentagonal prisms with $\text{Cl}\cdots\text{N}$ distances in the range 4.50–6.80 Å, (Figs. 4 and 5). The perchlorates with the cubic coordination are those anions which show highest disorder in the structure.

One of the differences between the nitrogen and oxygen bases is the number of the electron lone-pairs. In amine oxide the electron lone-pair of the nitrogen atom of the tertiary amines is bonded to the oxygen atom by co-ordinate covalence, and is usually expressed by the following formulas [9]:

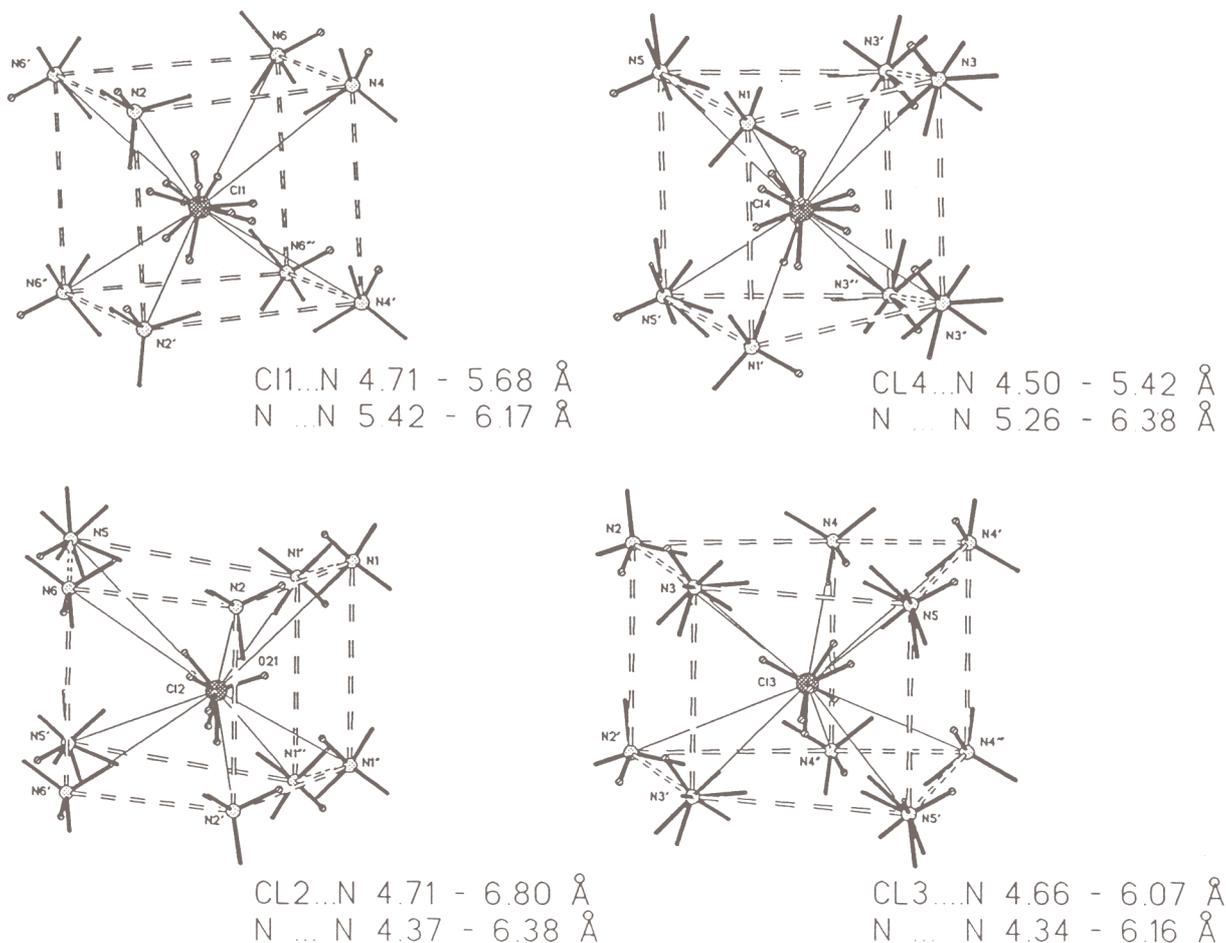


Hence amine oxides can form hydrogen-bonded complexes of various composition. Owing to two electron lone-pairs on the oxygen atom, amine oxides can directly interact with one or two proton donors and the following structures are probable [10–12]:



One of the most controversial questions about H-bond geometries is whether bonds tend to form along lone-pair directions (i.e., are motifs 4 and 7 more stable than motifs 5 and 8, respectively)? The H-bond geometry is strongly related to the type of the oxygen hybridization. In the case of carbonyl groups there is a statistically significant tendency for $\text{N}-\text{H}\cdots\text{C}=\text{O}$ bonds to form in, or near to, the directions of the sp^2 lone-pairs [12].

In the crystalline complexes with two proton-donors motif 6 was recognized, e.g. in trimethylamine *N*-oxide dihydrate [8], hydrates of several,

Fig. 4. Coordination polyhedra around the ClO_4^- anions.

N, N' -dioxides [8], 1:2 complexes of substituted pyridine N -oxides with pentachlorophenol [13]. The amide carbonyl group can also interact with two proton donors to form species similar to motif **6** [11]. The common feature of motif **6** is coplanarity with linear hydrogen bonds. In the investigated 3:2 complex one of the cations is nearly planar with the following angles: $\text{O}(1)\text{--O}(2)\text{--O}(3) = 110.7(2)^\circ$; $\text{O}(1)\text{--O}(2)\text{--N}(2) = 133.8(2)^\circ$ and $\text{O}(3)\text{--O}(2)\text{--N}(2) = 113.8(2)^\circ$. The second cation has slightly different geometries [$\text{O}(4)\text{--O}(5)\text{--O}(6) = 89.7(2)^\circ$; $\text{O}(6)\text{--O}(5)\text{--N}(5) = 126.8(2)^\circ$ and $\text{O}(4)\text{--O}(5)\text{--N}(5) = 125.6(2)^\circ$] and is not quite planar; the $\text{O}(5)$ atom is $0.471(4)$ Å above the plane drawn through atoms $\text{O}(4)$, $\text{N}(5)$ and $\text{O}(6)$. Thus in the 3:2 complex the

$\text{O} \cdots \text{HO}$ bonds are formed in, or near to, the directions of the two electron lone-pairs.

The present results agree with the general rule that bonds involving single acceptors (i.e. $\text{C}=\text{O}$ or $\text{N}\text{--O}$ groups that only accept one hydrogen bond $\text{X} \rightarrow \text{O} \cdots \text{HA}$) are shorter than those involving two or more acceptors (e.g. motif **5**) [12].

3.2. Infrared spectra

The IR spectrum shows that in the 1:1 complex of trimethylamine N -oxide the oxygen atom is protonated resulting in OH stretching vibration near 3260 cm^{-1} (Fig. 6(a)). The spectrum of the 2:1 complex shows a very intense and broad absorption

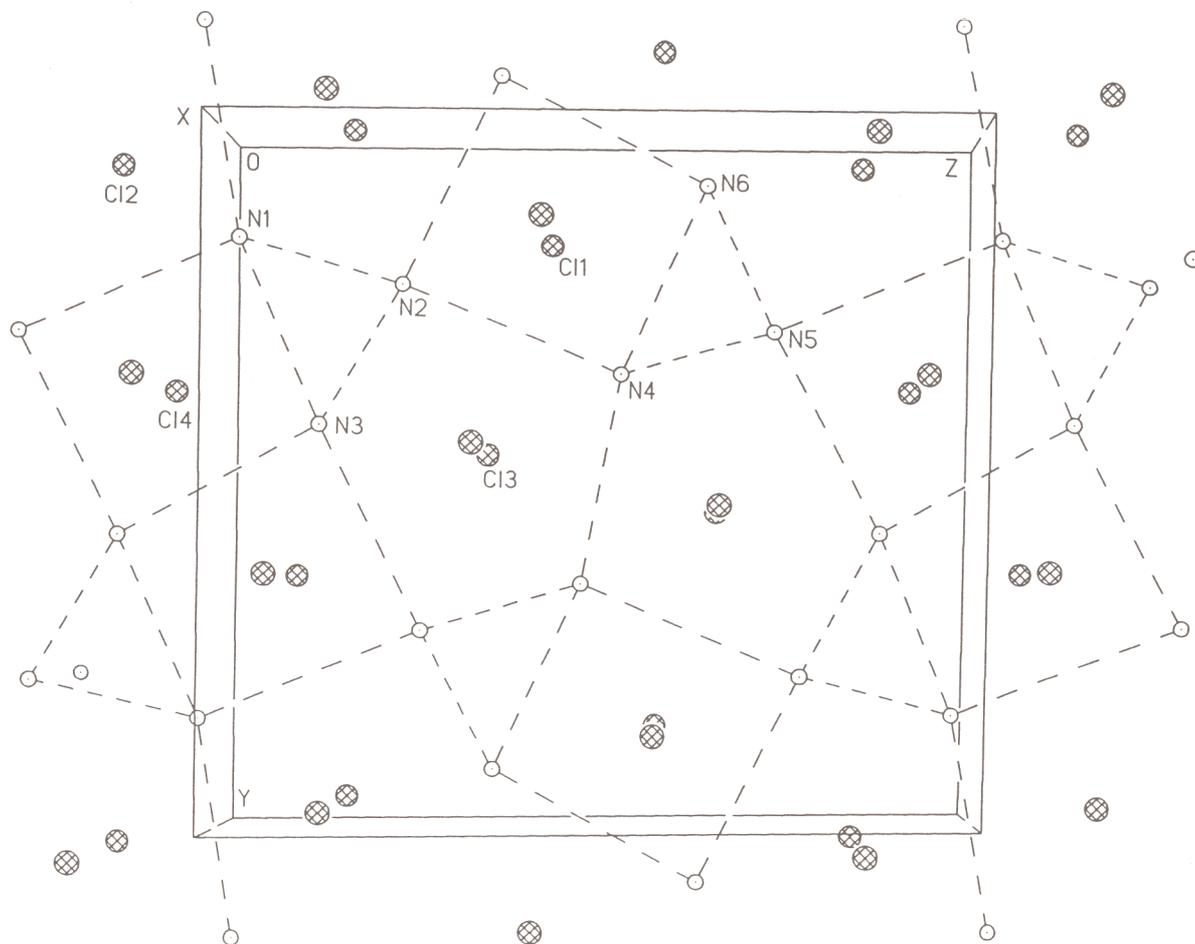


Fig. 5. Arrangement of the coordination polyhedra in the crystal.

within the $1600\text{--}400\text{ cm}^{-1}$ region, which appears instead of the usual OH stretching band in the higher frequency region (Fig. 6(b)). This absorption is a very characteristic feature of short OHO bonds [14]. As the H-bonds of the 3:2 complex are longer than that in the 2:1 complex, but shorter than that in the 1:1 complex, its spectrum is totally different from those of the 1:1 and 2:1 complexes. The most characteristic feature of the 3:2 complex in the solid state are two broad bands near 2530 and 1810 cm^{-1} (Fig. 6(c)). The spectra of the 1:1 and 2:1 complexes in acetonitrile are similar to those in the solid state, while the spectrum of the 3:2 complex is completely different. It is a sum of absorption of the 1:1 and 2:1 complexes. The IR

spectra of the 1:1, 2:1 and 3:2 complexes of 4-NMe₂-2,6-Me₂-pyridine *N*-oxide with perchloric acid (Fig. 7) are very similar to those of trimethylamine *N*-oxide. The spectrum of the 3:2 complex in acetonitrile is also a sum of absorption of the 1:1 and 2:1 complexes. Hence, the 3:1 complexes are not stable in acetonitrile solution.

In the region $2700\text{--}1700\text{ cm}^{-1}$ two broad bands are found with $(\text{Me}_3\text{NO})_3 \cdot (\text{HClO}_4)_2$ and only one band with $(4\text{-NMe}_2\text{-2,6-Me}_2\text{C}_5\text{H}_2\text{NO})_3 \cdot (\text{HClO}_4)_2$ in the solid state. The splitting of absorption in the former compound is probably caused by the Fermi resonance [15]. Analogous but reverse situation was observed in complexes of the type $(\text{N-H}\cdots\text{H})^+ \text{ClO}_4^-$, a single band is found in

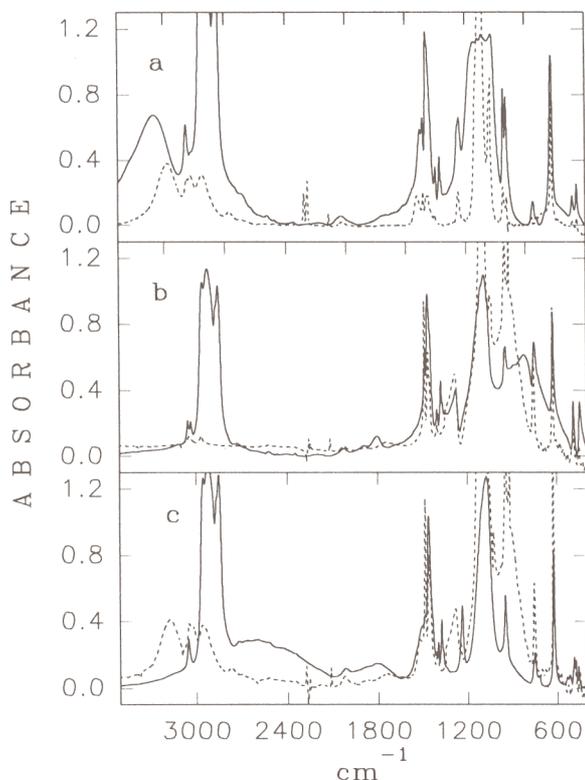


Fig. 6. FTIR spectra of (a) $\text{Me}_3\text{NO} \cdot \text{HClO}_4$; (b) $(\text{Me}_3\text{NO})_2 \cdot \text{HClO}_4$; (c) $(\text{Me}_3\text{NO})_3 \cdot (\text{HClO}_4)_2$ (—) in Nujol; (---) in $\text{CH}_3\text{CN}/\text{CD}_3\text{CN}$.

hemiperchlorates of tertiary amines and two bands in hemiperchlorates of 5- and 6-membered aromatic heterocycles [16].

4. Conclusions

The X-ray data for $(\text{Me}_3\text{NO})_3 \cdot (\text{HClO}_4)_2$ show that the oxygen atom of a central trimethylamine *N*-oxide molecule accepts hydrogen bonds from two protonated trimethylamine *N*-oxide cations with $\text{O} \cdots \text{O}$ distances in the range 2.537(5)–2.562(7) Å. Both $\text{O} \cdots \text{H}-\text{O}$ bonds are linear and formed in, or near to, the directions of the electron lone-pairs of the oxygen atom (motif 6). The structure is stable in the crystal. In acetonitrile solutions, the 3:2 complexes of trimethylamine *N*-oxide and 4-dimethylamine-2,6-dimethylpyridine *N*-oxide exist

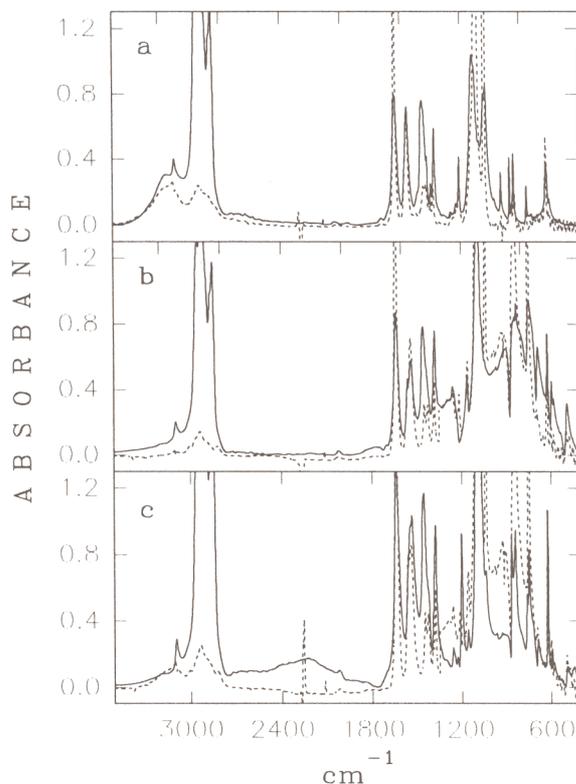


Fig. 7. FTIR spectra of (a) $4\text{-NMe}_2\text{-2,6-Me}_2\text{C}_5\text{H}_2\text{NO} \cdot \text{HClO}_4$; (b) $(4\text{-NMe}_2\text{-2,6-Me}_2\text{C}_5\text{H}_2\text{NO})_2 \cdot \text{HClO}_4$; (c) $(4\text{-NMe}_2\text{-2,6-Me}_2\text{C}_5\text{H}_2\text{NO})_3 \cdot (\text{HClO}_4)_2$, (—) in Nujol; (---) in $\text{CH}_3\text{CN}/\text{CD}_3\text{CN}$.

as a mixture of the 1:1 and 2:1 complexes. This suggests that the 3:2 complexes are stabilized by the lattice energy.

Acknowledgement

This work was supported in part by the State Committee of Scientific Research (KBN), grant 2P 303 06907.

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