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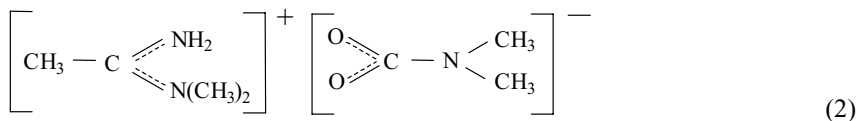
Crystal Structure of N^2,N^2 -Dimethylacetamidinium N,N -Dimethylcarbamate

The title compound crystallizes in the monoclinic space group $P2_1/c$ with four formula units in a unit cell of dimensions $a = 10.814(2)$, $b = 8.400(2)$, $c = 11.398(4)$ Å, $\beta = 110.86(2)^\circ$, $V = 967.5(5)$ Å³. The crystal structure is characterized by almost exactly planar $[\text{Me}_2\text{NC}(\text{NH}_2)\text{Me}]^+$ cations and $[\text{O}_2\text{CNMe}_2]^-$ anions which are approximately perpendicular oriented to one another. The amidine $\text{N}^1\text{--C}$ and $\text{N}^2\text{--C}$ bond lengths are significantly different (1.341(7) and 1.292(7) Å, respectively) but the C--O distances of the carbamate anion are equal within experimental error (1.263(6) and 1.256(6) Å). An essential feature of the crystal structure are $\text{N--H}\cdots\text{O}$ hydrogen bonds between cations and anions.

Keywords: crystal structure, molecular structure, X-ray analysis, amidinium carbamate, hydrogen bonds

1. Introduction

Recently, we reported the reactions of the 1:1 adduct of dimethylamine and carbon dioxide (dimcarb) with metallic copper and zinc, respectively, giving N,N -dimethylcarbamato complexes of these metals (KLUNKER et al.). In this way, the complex $[\text{Cu}(\text{O}_2\text{CNMe}_2)_2(\text{NHMe}_2)_2]$ (**1**) was prepared and structurally characterized by X-ray analysis. By addition of metallic copper to an oxygen-free solution of **1** in a dimcarb-acetonitrile mixture colourless and strongly hygroscopic crystals of an initially unknown substance were obtained. That substance could be undoubtedly identified by X-ray analysis and proved to be N,N -dimethylacetamidinium N,N -dimethylcarbamate $[\text{Me}_2\text{NC}(\text{NH}_2)\text{Me}]^+[\text{O}_2\text{CNMe}_2]^-$ (**2**). Apparently, **1** reacts with metallic copper to a copper(I) complex which catalyzes the addition of acetonitrile to dimethylamine (ROUSSELET et al.) and N,N -dimethylacetamidine $\text{Me}_2\text{NC}(\text{NH})\text{Me}$ formed in this way is precipitated in form of **2**.



Amidines are of actual and widespread interest because of their biological and pharmaceutical effects and their ligand properties in coordination chemistry. Therefore, a number of crystal structure investigations on amidines have been performed (BARKER, POWELL, 1996; BARKER, POWELL, 1998, and related references given in both papers). But on checking the January 1998 version of the Cambridge Structural Database (ALLEN et al.)

it appeared that the crystal structure of **2** was unknown up to now. As a result of our investigation it will be described in this paper.

Parameter	2
Empirical formula	C ₇ H ₁₇ N ₃ O ₂
Molecular mass [g mol ⁻¹]	175.24
Crystal system	monoclinic
Space group	P2 ₁ /c
Lattice parameters	
a [Å]	10.814(2)
b [Å]	8.400(2)
c [Å]	11.398(4)
α [°]	90.0
β [°]	110.86(2)
γ [°]	90.0
V [Å ³]	967.5(5)
Z	4
F(000)	384
D _{calc.} [g cm ⁻³]	1.203
μ(MoKα) [mm ⁻¹]	0.089
Intensity variation [%]	5.4
2θ _{max.} [°]	50.0
hkl range	-12/12, 0/9, -13/0 and - 12/12, -9/0, 0/13
Measured reflections	3394
Unique reflections	1697
R _{int.}	0.0910
Observed reflections (I > 2σ(I))	846
Refined parameters	119
Weighting coefficients a / b [a]	0.0754 / 1.5637
R1 / wR2 / S (I > 2σ(I))	0.0820 / 0.1777 / 1.217
(Δ/σ) _{max.} in last l.s. cycle	0.000
Δρ _{fin.} (min. / max.) [e Å ⁻³]	-0.308 / 0.370

Table 1: Crystal data and details of X-ray structure analysis of **2**

$$^{[a]} w = \frac{1}{\left[\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P \right]} \quad \text{where} \quad P = \frac{1}{3}(F_o^2 + 2F_c^2).$$

2. Experimental

Only rather small single crystals of **2** were obtained by a method described earlier (KLUNKER et al.). A colourless crystal of the size 0.10 x 0.10 x 0.20 mm as the best of all checked specimens was mounted on a Stoe STADI4 diffractometer equipped with an Oxford Cryosystems Cryostream apparatus. All measurements were performed at 200 K using graphite-monochromatized MoKα radiation (λ = 0.71073 Å). Lattice constants were derived from a least-squares treatment of the setting angles for 84 reflections in the θ range 8.0 - 12.5 °. Intensity data were collected in the ω/2θ scanning mode and corrected for

Lorentz and polarization effects but absorption effects were neglected. The structure was solved by direct methods (program SHELXS-86 (SHELDRICK, 1986)). Structure refinement on F^2 was performed using the full-matrix least-squares techniques of SHELXL-93 (SHELDRICK, 1993) with anisotropic displacement parameters for the non-H atoms. The two hydrogen atoms bonded to nitrogen could be detected in a difference Fourier map but the other ones were placed at their idealized positions. The hydrogen atomic parameters were refined isotropically according to the riding model. Figures 2 and 3 were plotted by use of Siemens XP (XP/PC).

atom	x/a	y/b	z/c	U_{eq}
O1	0.1931(3)	0.1094(5)	0.4575(3)	0.041(2)
O2	0.2671(4)	-0.0503(5)	0.6248(4)	0.046(2)
N1	0.4043(4)	0.1303(6)	0.5903(4)	0.048(2)
C1	0.2823(5)	0.0585(7)	0.5556(5)	0.035(2)
C2	0.5140(6)	0.0789(9)	0.6997(6)	0.065(3)
C3	0.4347(6)	0.2484(8)	0.5124(6)	0.059(3)
N3	-0.0269(5)	0.2130(6)	0.5067(4)	0.034(2)
N2	-0.0889(4)	0.3872(6)	0.6316(4)	0.040(2)
C4	-0.0611(6)	0.5233(7)	0.7183(5)	0.038(2)
C5	-0.2256(5)	0.3272(8)	0.5818(6)	0.048(2)
C6	0.0005(5)	0.3291(7)	0.5930(5)	0.038(2)
C7	0.1401(5)	0.3904(7)	0.6464(5)	0.034(2)

Table 2: Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for non-H atoms in **2** (esd's in parentheses)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} \mathbf{a}_i \mathbf{a}_j \mathbf{a}_i^* \mathbf{a}_j^*$$

A summary of crystal data along with details of the structure determination is given in Table 1. The rather high values for R_1 and R_{int} as well as the great number of unobserved reflections (cf. Table 1) are attributed to the small size and the poor quality of the single crystal used for intensity measurements. Final atomic parameters are listed in Table 2.

Further details of the X-ray investigation are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, quoting the depository number CSD-410380.

3. Results and discussion

The molecular structure of the title compound **2** including used atomic numbering is illustrated in Fig. 1. Bond lengths and angles are summarized in Table 3.

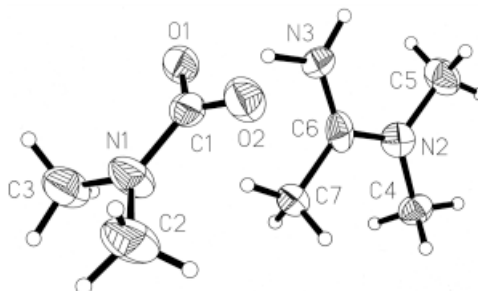


Fig. 1: Molecular structure and atomic labeling scheme for the pair of ions in $[\text{Me}_2\text{NC}(\text{NH}_2)\text{Me}]^+ [\text{O}_2\text{CNMe}_2]^-$ (**2**). Displacement ellipsoids are drawn at the 50% probability level and H atoms as small circles of arbitrary size.

atoms	bond lengths	atoms	angles
O1–C1	1.263(6)	C1–N1–C3	122.0(5)
O2–C1	1.256(6)	C1–N1–C2	121.7(5)
N1–C1	1.374(7)	C3–N1–C2	115.9(5)
N1–C3	1.445(7)	O2–C1–O1	125.0(5)
N1–C2	1.448(7)	O2–C1–N1	117.7(5)
N3–C6	1.341(7)	O1–C1–N1	117.3(5)
N2–C6	1.292(7)	C6–N2–C4	121.6(5)
N2–C4	1.471(7)	C6–N2–C5	120.7(5)
N2–C5	1.471(7)	C4–N2–C5	117.5(5)
C6–C7	1.503(7)	N2–C6–N3	121.9(5)
		N2–C6–C7	119.9(5)
		N3–C6–C7	118.3(5)

Table 3: Bond lengths (Å) and bond angles (°) in **2** (esd's in parentheses)

The crystal structure of **2** consists of dimethylacetamidinium [$\text{Me}_2\text{NC}(\text{NH}_2)\text{Me}$]⁺ cations and dimethylcarbamate [O_2CNMe_2]⁻ anions. The non-hydrogen atomic skeleton of each ion is planar in very good approximation; the maximum deviation from planarity amounts to 0.042(6) Å (atom C4) and 0.040(5) Å (atom N1), respectively. The l.s. planes of cation and anion are almost perpendicular oriented to another (interplanar angle 92.4°).

Of special interest are the two N–C bond lengths of the central amidinium fragment. They are significantly different [N2–C6 = 1.292(7) Å, N3–C6 = 1.341(7) Å] indicating different bond orders. Application of a semiempirical correlation $r = r_0 - 0.18 p$ (NORRESTAM et al.) between π -bond order p and bond length r , where r_0 is a standard single bond length [1.458 Å for N–C, 1.517 Å for C–C] gives the following π -bond orders in the cation of **2**: 0.92, 0.65 and 0.09 for N2–C6, N3–C6 and C6–C7, respectively. Therefore, N2–C6 is a typical N(sp²)–C(sp²) double bond whereas N3–C6 is intermediate between a single and a double bond. The just mentioned values for the N–C bond lengths and their difference of 0.049(7) Å found in **2** resemble those in acetamide (1.298(1) and 1.344(1) Å, NORRESTAM et al.), *N,N*-diphenylbenzamide (1.302(7) and 1.360(8) Å, ALCOCK et al.), *N*²-*p*-Nitrophenylbenzamide (1.280(5) and 1.355(5) Å, SURMA et al.), *N*²-(*m*-chlorophenyl)-*N*²,*N*¹-pentamethylenebenzamide (1.290(6) and 1.365(6) Å, TYKARSKA et al., 1986a), *N*²-(*p*-methoxyphenyl)-*N*²,*N*¹-pentamethylenebenzamide (1.283(5) and 1.372(5) Å, TYKARSKA et al., 1986b) and the three strongly related compounds *N*²,*N*¹-dimethyl-*N*²-*p*-nitrophenylform-, -acet- and -2,2-dimethylpropanamide (ranges 1.281(5) - 1.294(5) and 1.331(4) - 1.380(3) Å, CISZAK et al.). In contrast to that, much smaller or even insignificant differences were observed in acetamidinium chloride (1.305(2) and 1.310(3) Å, CANNON et al.), isopropylamidinium chloride (1.299(6) and 1.320(5) Å, BARKER et al., 1996), cyclopropylcarboxamidinium chloride (1.304(4) and 1.316(4) Å, BARKER et al., 1998) and bis(acetamidinium) carbonate monohydrate (1.307(5) and 1.315(5) Å, NORRESTAM, 1984).

An inspection of the just given values from literature shows that the differentiation into imino and amino function manifested by different N–C bond lengths is only perceptible in the case of neutral amidines but not in the case of protonated amidines (amidinium cations). The significantly different N–C bond lengths in the cation of **2** disagree with this general tendency.

As already mentioned above, the non-hydrogen atomic skeleton of the carbamate anion is nearly exactly planar. Within the 3 σ criterion the observed bond lengths and angles are in agreement with C_{2v} symmetry and the torsion angles around N1–C2 deviate no more than 6°

($C3-N1-C1-O1 = -6.0(6)^\circ$) from the ideal values 0 and 180° , respectively. Bond lengths $C1-O1 = 1.263(6)$ Å and $C1-O2 = 1.256(6)$ Å are somewhat shorter and $C1-N1 = 1.374(7)$ Å a little longer than the corresponding distances found in ammonium carbamate ($1.279(5)$, $1.289(5)$ and $1.361(5)$ Å, respectively, ADAMS et al.).

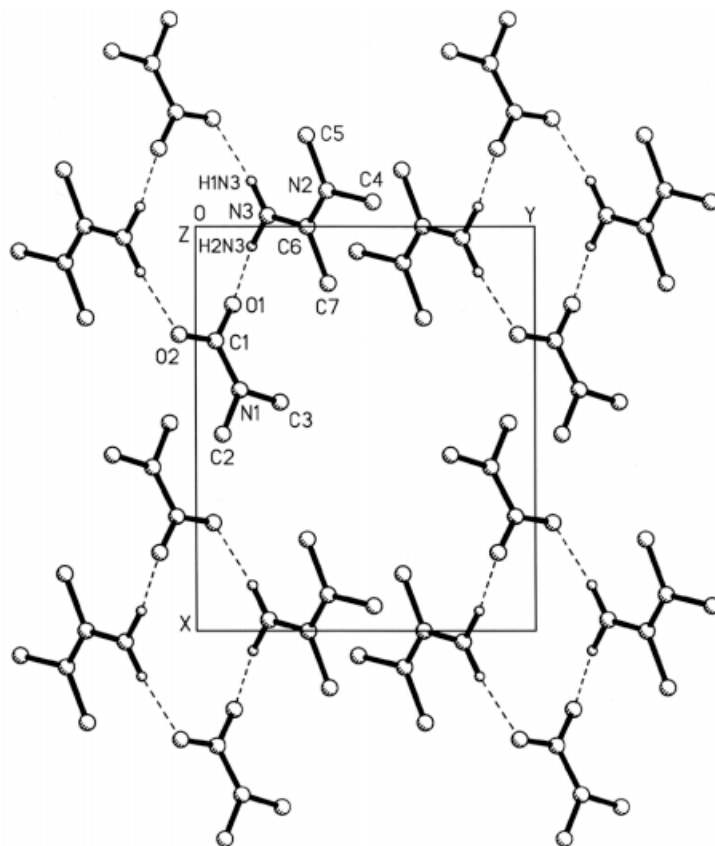


Fig. 2: Crystal structure of **2** projected along [001]. For clarity, structural motifs referring to the c -glide plane and the 2_1 -axis as well as the H atoms of the methyl groups are omitted. Broken lines represent hydrogen bonds.

An essential feature of the crystal structure of **2** (Fig. 2) is the formation of centrosymmetric cyclic clusters consisting of two cations and two anions which are connected by hydrogen bonds between the NH protons of the amidinium cation and the carboxylic oxygen atoms of the carbamate anion. The N–H \cdots O bonds are of moderate strength, the N \cdots O distances ($N3\cdots O1 = 2.771(6)$ Å, $N3\cdots O2 = 2.844(6)$ Å) are in the normal range given in the literature for hydrogen bonds of this type (JEFFREY). The geometric parameters of the hydrogen bonds are summarized in Table 4.

D–H \cdots A	D \cdots A (Å)	D–H (Å)	A \cdots H (Å)	D–H \cdots A ($^\circ$)
N3–H2N3–O1	2.771(6)	1.05(8)	1.73(8)	169(6)
N3–H1N3–O2#1	2.844(6)	0.96(6)	1.90(6)	171(5)

Table 4: Hydrogen bonding geometry in the crystal structure of **2** (esd's in parentheses)

#1: $-x, -y, 1-z$

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