Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Betainohydroxamic acid chloride

Dubravka Matković-Čalogović,[a] Erim Bešić,[b] Mladen Biruš[b] and Mario Gabričević[b]*

[a]Laboratory of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Ul. kralja Zvonimira 8, 10000 Zagreb, Croatia, and [b]Laboratory of General and Inorganic Chemistry, Faculty of Pharmacy and Biochemistry, University of Zagreb, A. Kovačića 1, 10000 Zagreb, Croatia
Correspondence e-mail: mariog@pharma.hr

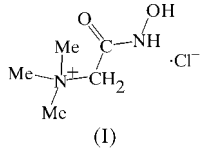
Received 27 October 2003
Accepted 29 October 2003
Online 14 November 2003

The title compound, *N*-hydroxy-2-(trimethylammonio)acetamide chloride, $C_5H_{13}N_2O_2^+\cdot Cl^-$, has been synthesized and structurally characterized. The structure consists of betainohydroxamic acid cations and Cl^- anions linked by N—H···Cl and O—H···Cl hydrogen bonds into chains along [001]. It was found that the positive inductive effect of the charged N atom in close proximity to the hydroxamate carbonyl O atom has a negligible effect on the hydroxamic C—N bond length.

Comment

Hydroxamic acids are weak organic acids with a variety of applications in extractive metallurgy, in pharmaceuticals, as food additives, *etc*. (Kaczka *et al.*, 1962; Matzanke *et al.*, 1989; Hershko *et al.*, 1992; Rogers, 1987; Ghio *et al.*, 1992). Their importance and applications primarily originate from their ability to form stable metal-ion binding sites (Crumbliss, 1991).

It was recently found that the rotation about the hydroxamate C—N bond in desferrioxamine B and *N*-methylacetohydroxamic acid is slow enough to be measured by dynamic NMR spectroscopy at room temperature (Biruš *et al.*, 1995, 1999). The rotation-rate constant was found to be *ca* $3\ s^{-1}$ at 298 K. On the other hand, the rotation rate for acetohydroxamic acid was too fast to be measured by dynamic ^1H or ^{13}C NMR spectroscopy. The C and N substituents of the hydroxamic functionality have a major influence on the rotation rate, since they may increase or decrease the partial double-bond character of the hydroxamate C—N bond through their electron-donating or electron-withdrawing character. This, in turn, may cause a corresponding shortening or lengthening of the C—N bond. It seemed worthwhile to examine whether the positive inductive effect exerted by the positively charged N atom in betainohydroxamic acid would exhibit any effect on the length of the C—N bond. If the positive charges in close proximity to the carbonyl O atom are able to stabilize the enolate ion formed by an electron density shift from the hydroxamate-N free electron pair into the C—N bond, the partial double-bond character of the C—N bond would increase and shortening of that bond could possibly be observed. In the light of this interest, we present here the synthesis and crystal structure of betainohydroxamic acid chloride, (I).



(I)

The structure of (I) consists of cations of betainohydroxamic acid and Cl^- anions. The crystal structure parameters can be compared with the crystal data reported for some other monohydroxamic acids. It appears that, within experimental error, the length of the hydroxamate C—N bond does not change upon substitution of the methyl H atom in acetohydroxamic acid hemihydrate [1.333 (6) Å; Bracher & Small, 1970] with the charged N atom in (I) [N2—C5 =

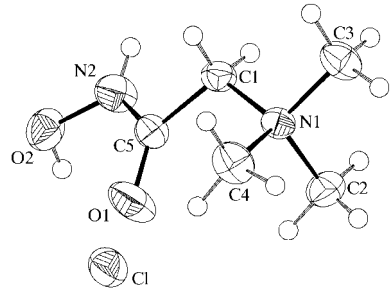


Figure 1
A view of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

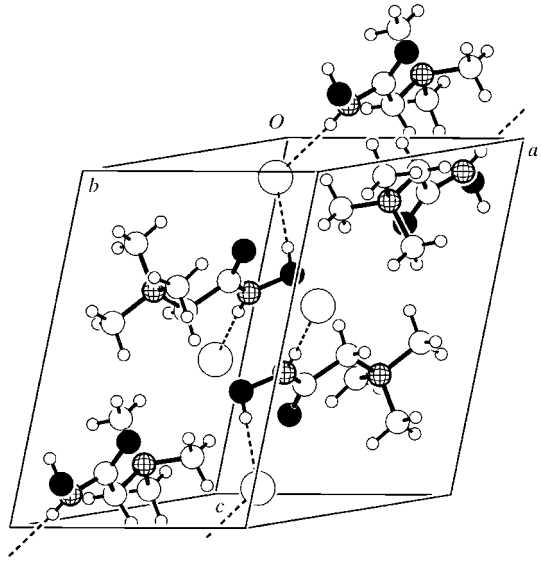


Figure 2
The packing of the ions in the unit cell of (I). Hydrogen bonds are indicated by dashed lines.

  DOI: 10.1107/S0108270103024867

1.327 (1) Å]. Some other bond distances in (I) can also be compared with the analogous bond distances in aceto-hydroxamic and salicylohydroxamic acid (Larsen, 1978). For instance, the C═O bond in the betainohydroxamic acid cation [1.225 (1) Å] is slightly shorter then the corresponding bonds in acetohydroxamic acid [1.245 (6) Å] and salicylohydroxamic acid [1.258 (4) Å], since this O atom is not involved in hydrogen bonding in (I), whereas in the other two structures it is an acceptor for two hydrogen bonds. The N—O distances in betaino-, salicylo- and acetohydroxamic acids all appear to be equal within the range of experimental error [1.395 (1), 1.390 (4) and 1.400 (5) Å, respectively].

It seems that the positive inductive effect of the charged N atom in close proximity to the hydroxamate carbonyl O atom has a small effect on the hydroxamic C—N bond length. Both hydrogen-bond donor atoms, O2 and N2, are involved in hydrogen bonding with the Cl^- anion, linking the ions into chains along [001].

Experimental

Betainohydroxamic acid chloride was prepared according to the published procedure of Biruš *et al.* (1984). Its purity was confirmed by ^{1}H NMR spectroscopy and by titration with a standardized solution of NaOH. Single crystals of (I) were grown from a saturated solution of betainohydroxamic acid chloride in ethanol, by slow evaporation in a thermostatic oven at 310 K; the beaker containing the solution was covered with aluminium foil to reduce evaporation. Crystals of (I) of good quality were obtained after two weeks, and these were stable for months when exposed to the atmosphere.

Crystal data

$C_5H_{13}N_2O_2^+\cdot Cl^-$
M_r = 168.62
Monoclinic, $P2_1/c$
a = 9.1099 (9) Å
b = 8.8472 (13) Å
c = 11.0093 (11) Å
β = 110.182 (6)°
V = 832.84 (17) Å^3
Z = 4
D_x = 1.345 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 45 reflections
θ = 10.0–17.7°
μ = 0.41 mm^{-1}
T = 295.0 (10) K
Block, colourless
0.45 × 0.23 × 0.17 mm

Data collection

Philips PW1100 diffractometer, updated by Stoe
$\theta/2\theta$ scans
4778 measured reflections
2389 independent reflections
1324 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 30.0°
$h = -12 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -15 \rightarrow 15$
4 standard reflections
frequency: 90 min
intensity decay: 2.3%

Table 1
Selected geometric parameters (Å, °).

O1—C5	1.2248 (12)	N1—C3	1.5085 (13)
O2—N2	1.3949 (13)	N1—C4	1.5090 (12)
N1—C1	1.5001 (13)	N2—C5	1.3266 (14)
N1—C2	1.5076 (12)	C1—C5	1.5306 (14)
C1—N1—C2	110.61 (8)	C5—N2—O2	119.42 (9)
C1—N1—C3	107.76 (8)	N1—C1—C5	114.38 (8)
C2—N1—C3	108.26 (9)	O1—C5—N2	123.81 (10)
C1—N1—C4	111.90 (8)	O1—C5—C1	124.44 (9)
C2—N1—C4	110.10 (8)	N2—C5—C1	111.75 (8)
C3—N1—C4	108.08 (9)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H1···Cl	0.803 (18)	2.210 (18)	3.0083 (11)	172.8 (19)
N2—H2···Cl^{i}	0.839 (17)	2.313 (17)	3.1479 (13)	173.2 (12)

Symmetry code: (i) $x, \frac{1}{2}-y, \frac{1}{2}+z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.082
S = 1.00
2389 reflections
144 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0457P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.009 (4)

H atoms were found in a difference Fourier map and were refined isotropically, giving C—H distances in the range 0.87 (1)–0.99 (1) Å.

Data collection: *STADI*4 (Stoe & Cie, 1995); cell refinement: *X-RED* (Stoe & Cie, 1995); data reduction: *X-RED*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON*98 (Spek, 1990); software used to prepare material for publication: *SHELXL*97.

The authors thank the Ministry of Science and Technology of the Republic of Croatia for financial support (grant Nos. 0006441 and 0119632).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1624). Services for accessing these data are described at the back of the journal.

References

Biruš, M., Gabričević, M., Kronja, O. & Klaić, B. (1995). *Inorg. Chem.* **34**, 3110–3113.
Biruš, M., Gabričević, M., Kronja, O., Klaić, B., van Eldik, R. & Zahl, A. (1999). *Inorg. Chem.* **38**, 4064–4069.
Biruš, M., Kujundžić, N., Pribanić, M. & Tabor, Z. (1984). *Croat. Chem. Acta*, **57**, 313–324.
Bracher, B. H. & Small, R. W. H. (1970). *Acta Cryst.* B**26**, 1705–1709.
Crumbliss, A. L. (1991). *Handbook of Microbial Iron Chelates*, edited by G. Winkelman, pp. 177–233. Boca Raton: CRC Press.
Ghio, A. J., Kennedy, T. P., Whorton, R. A., Crumbliss, A. L., Hatch, G. E. & Hoidal, J. R. (1992). *Am. J. Physiol.* **263**, 511–518.
Hershko, C., Gordeuk, V. R., Thuma, P. E., Thenacho, E. N., Spira, D. T., Hider, R. C., Peto, T. E. A. & Drittenham, G. M. (1992). *J. Inorg. Biochem.* **47**, 267–277.
Kaczka, E. A., Gitterman, C. O., Dulaney, E. L. & Folkers, K. (1962). *Biochemistry*, **1**, 340–343.
Larsen, I. K. (1978). *Acta Cryst.* B**34**, 962–964.
Matzanke, B. F., Mueller-Matzanke, G. & Raymond, K. N. (1989). *Iron Carriers and Iron Proteins*, Vol. 5, edited by T. M. Loehr, pp. 1–121. New York: VCH Publishers.
Rogers, H. J. (1987). *Iron Transport in Microbes, Plants, and Animals*, edited by G. Winkelmann, D. Van der Helm & J. B. Nielands, pp. 223–233. New York: VCH Publishers.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Stoe & Cie (1995). *STADI*4 (Version 1.05b) and *X-RED* (Version 1.05b). Stoe & Cie, Darmstadt, Germany.