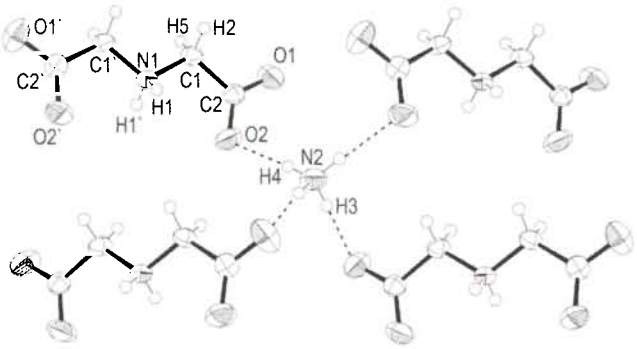
Crystal structure of ammonium iminodiacetate, $NH_4C_4H_6NO_4$

Z. B. Markovic*,[I], G. A. Bogdanovic[II,I], A. Spasojevic-de Biré[II], T. J. Sabo[III] and S. R. Trifunovic[III]

[I] University of Montenegro, Faculty of Metallurgy and Technology, Cetinjski put b.b., 81000 Podgorica, Yugoslavia
[II] Ecole Centrale Paris, Laboratoire Structures, Proprietes et Modelisation des Solides, UMR 8580 du CNRS, Grande Voie des Vignes, F-92295 Châtenay-Malabry Cedex, France
[III] University of Kragujevac, Faculty of Science, Department of Chemistry, R. Domanovica 12, PO Box 60, 34000 Kragujevac, Yugoslavia

Received October 29, 1999, CCDC-No. 1267/324



Abstract

$C_4H_{10}N_2O_4$, orthorhombic, *Pccn* (No. 56), $a = 7.782(2)$ Å, $b = 8.642(2)$ Å, $c = 10.230(3)$ Å, $V = 688.0$ Å^3, $Z = 4$, $R_{gt}(F) = 0.071$, $wR_{ref}(F^2) = 0.215$, $T = 293$ K.

Source of material

Molecular structure of imino-diacetic acid (3-azapentane-1,5-dicarboxylic acid) as well as its hydrohalogenide derivates, was determined crystallographically [1-4]. In this work, its monoammonium salt as supple colorless crystals, suitable for X-ray analysis, was prepared from mother water-methanol mixture of ammonia, imino-diacetic acid and carbondisulfide in a try to prepare the corresponding dithiocarboxy derivate of the iminodiacetic acid.

Discussion

Most iminodiacetic derivates synthesized so far are in the form of positively charged iminodiacetic acid ions, $[C_4H_8NO_4]^+$ [1-3], or in the form of neutral iminodiacetic acid, $C_4H_7NO_4$ [4]. In this paper, we report the sythesis and crystal strcture of ammonium iminodiacetate with negatively charged $[C_4H_6NO_4]^-$. Except for carboxylate groups, related interatomic distances and angles are not significantly different in comparison to $[C_4H_8NO_4]^+$ and $C_4H_7NO_4$. The negative charge is most probably spread over the carboxylate groups O1–C2–O2 and O1′–C2′–O2′. The C2—O1 bond length (1.253(3) Å) is somewhat longer than the C2—O2 bond (1.242(3) Å). This is probably due to the fact that O1 accepts two hydrogen bonds while O2 only one. All ammonium and iminodiacetate ions are included in the three-dimensional network of hydrogen bonds. Every N2 atom is hydrogen bonded to four oxygen atoms, and all of them are related to four different symetrical iminodiacetate groups: N2(*i*)···O2(*i*) = 2.859(2) Å, H3(*i*)···O2(*i*) = 1.98(4) Å, ∠N2(*i*)–H3(*i*)···O2(*i*) = 175(3)°; N2(*i*)···O2(*ii*) = 2.859(2) Å, H3(*ii*)···O2(*ii*) = 1.98(4) Å, ∠N2(*i*)–H3(*ii*)···O2(*ii*) = 175(3)°; N2(*i*)···O1(*iii*) = 2.749(3) Å, H3(*i*)···O1(*iii*) = 1.85(3) Å, ∠N2(*i*)–H3(*i*)···O2(*iii*) = 166(3)°; N2(*i*)···O1(*iv*) = 2.749(3) Å, H3(*ii*)···O1(*iv*) = 1.85(3) Å, ∠N2(*i*)–H3(*ii*)···O2(*iv*) = 166(3)°; (symmetry codes: (*i*) *x*,y,z;(*ii*) -*x*+0.5, –*y*+0.5, *z*; (*iii*) *x*, –*y*+0.5, *z*+0.5; (iv) –*x*+0.5, *y*, *z*+0.5). Atom O1 is also hydrogen bonded to N1 (*x*,*y*,*z*): N1(*i*)···O1(*ii*) = 2.783(2) Å, H1(*i*)···O1(*ii*) = 1.93(3) Å, ∠N1(*i*)–H1(*i*)···O1(*ii*) = 167(2)°; N1(*i*)···O1(*iii*) = 2.783(2) Å, H1(*iv*)···O1(*iii*) = 1.93(3) Å, ∠N1(*i*)–H1(*iv*)···O1(*iii*) = 167(2)°; (symmetry codes: (i) *x*, y, z; (*ii*) *x*+0.5, –*y*, –*z*+0.5; (*iii*) –*x*, *y*+0.5, –*z*+0.5; (*iv*) –*x*+0.5, –*y*+0.5, *z*). The plan formed by O1,C2,N1,C2′,O1′ is planar, maximum displacement from the best plane doesn't exceed 0.0001 Å. But C1, C1′,O2 and O2′ deviate from this plane by –0.066(2) Å, +0.066(2) Å, +0.043(2) Å and –0.043(2) Å respectively. These positions of the C1 and C1′ atoms decrease repulsion between H atoms bonded to C1 and C1′.

Table 1. Data collection and handling.

Crystal:	colourless, prismatic, size 0.28 × 0.31 × 0.38 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.29 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD-4, ω/2θ
$2\theta_{max}$:	55.88°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2854, 998
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 599
$N(param)_{refined}$:	67
Programs:	PARST [5], SHELXS-97 [6], SHELXL-97 [7], ORTEP [8]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	8*e*	0.166(3)	–0.214(3)	0.270(2)	0.031(6)
H(2)	8*e*	0.217(4)	–0.080(4)	0.094(3)	0.052(8)
H(3)	8*e*	0.334(4)	0.291(4)	0.532(3)	0.055(8)
H(4)	8*e*	0.299(4)	0.174(4)	0.437(3)	0.056(8)
H(5)	8*e*	0.398(4)	–0.161(4)	0.083(3)	0.048(6)

* Correspondence author (e-mail: zorica@1.cis.cg.ac.yu)
[I] Permanent address: "Vinca" Institute of Nuclear Sciences, Laboratory of Theoretical Physics and Condensed Matter Physics, 11001 Belgrade, PO Box 522, Yugoslavia

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	4*d*	1/4	3/4	0.2232(2)	0.023(1)	0.033(1)	0.0215(9)	–0.0004(9)	0	0
C(1)	8*e*	0.3151(2)	–0.1207(2)	0.1432(2)	0.0303(9)	0.038(1)	0.0258(8)	–0.0063(8)	0.0014(7)	0.0033(7)
C(2)	8*e*	0.3970(2)	0.0048(2)	0.2256(2)	0.028(1)	0.036(1)	0.035(1)	–0.0016(8)	–0.0059(7)	0.0021(9)
O(1)	8*e*	0.4610(2)	0.1157(2)	0.1636(2)	0.051(1)	0.054(1)	0.057(1)	–0.0222(8)	–0.0251(8)	0.0170(9)
O(2)	8*e*	0.3952(3)	–0.0092(2)	0.3465(2)	0.080(1)	0.056(1)	0.0324(9)	–0.017(1)	–0.0014(7)	–0.0097(8)
N(2)	4*c*	1/4	1/4	0.4804(3)	0.048(2)	0.051(2)	0.030(1)	–0.008(2)	0	0

Acknowledgment. This work was financially supported by the Ministry for Science and Technology of the Republic Serbia.

References

1. Oskarsson, Å.: The crystal and molecular structures of iminodiacetic acid hydrochloride, $C_4H_7NO_4 \cdot HCl$ and iminodiacetic acid hydrobromide, $C_4H_7NO_4 \cdot HBr$. Acta Crystallogr. B**29** (1973) 1747-1751.
2. Oskarsson, Å.: The crystal and molecular structure of iminodiacetic acid hydroiodide, $C_4H_7NO_4 \cdot HI$. Acta Crystallogr. B**30** (1974) 780-785.
3. Oskarsson, Å.: The crystal and molecular structure of iminodiacetic acid hydrofluoride monohydrate, $C_4H_7NO_4 \cdot HF \cdot H_2O$, at –100° C. Acta Crystallogr. B**30** (1974) 1184-1188.
4. Boman, C.-E.; Herbertsson H.; Oskarsson, Å.: The crystal and molecular structure of a monoclinic phase of iminodiacetic acid. Acta Crystallogr. B**32** (1974) 378-382.
5. Nardelli, M.: PARST95 - an update to PARST: a system of Fortran routines for calculating molecular structure parameters from the results of crystal structure analyses. J. Appl. Crystallogr. **28** (1995) 659.
6. Sheldrick, G. M.: Phase annealing in SHELX-90: direct methods for larger structures. Acta Crystallogr. A**46** (1990) 467-473.
7. Sheldrick, G. M.: SHELXL97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
8. Burnett, M. N.; Johnson, C. K.: ORTEPIII. Report ORNL-6895. Oak Ridge National Laboratory, Tenessee, USA 1996.