



A NEW N,N-DIMETHYLBIGUANIDIUM DERIVATIVE – SYNTHESIS AND STRUCTURAL CHARACTERISATION

Rodica Olar *, Mihaela Badea and Dana Marinescu

abstract: A new N,N-dimethylbiguanidium derivative ($C_4H_{12}N_5)_2(NO_3)(ClO_4)$ has been synthesised and characterised by single crystal X-ray diffraction. The derivative crystallizes in the monoclinic C2/c space group and the N,N-dimethylbiguanidium cation is involved in hydrogen bonds both with other cations as well as nitrate and perchlorate anions.

key words: N,N-dimethylbiguanidium derivative; nitrate; perchlorate; single crystal.

received: May, 21, 2010

accepted: June 26, 2010

1. Introduction

Biguanide derivatives show both coordinative and biological properties. Among these N,N-dimethylbiguanide (DMBG) presents antimicrobial potential [1] beside that is known as glucose lowering agent [2], analgesic, antimalarial [3] as well as antimetabolite for organisms that inhibit the metabolism of folic acid [4].

Some complexes with N,N-dimethylbiguanide were recently prepared and demonstrated also a good antimicrobial activity [5-10]. Moreover nickel(II) and copper(II) complexes of type $M(DMBG)_2(ClO_4)_2$ were fully characterised by single crystal X-ray diffraction [10]. The molecular structures are also known for some N,N-dimethylbiguanidium derivatives as chloride [11], nitrate [12] and acetate [9].

In this paper it is presented data concerning a new specie $(HDMBG)_2(NO_3)(ClO_4)$ that represent the first mixed N,N-dimethylbiguanidium derivative reported. The crystal structure of compound was solved by single-crystal X-ray analysis.

2. Experimental

The compound was synthesized from commercially available starting materials used without further purification. Manganese perchlorate hexahydrate (Merck) was of analytical

* Department of Inorganic Chemistry, University of Bucharest, 90-92 Panduri St., Bucharest, Romania,
corresponding author e-mail: rodica_m_olar@yahoo.com

grade while N,N-dimethylbiguanidium nitrate was prepared as reported elsewhere [12]. IR spectra were recorded in KBr pellets with an FTIR-Biorad 135 instrument in the 400-4000 cm^{-1} range.

Elemental analyses (C,H,N) were performed with a Perkin Elmer PE 2400 instrument.

The compound was obtained as colorless block crystals by slow evaporation of the ethanol solution. During a few weeks standing at room temperature, crystals suitable for single-crystal X-ray diffraction studies were grown. Each single-crystal was mounted on a cryoloop. Data collection was realised at room temperature and processed using the program SMART [13] on a Bruker SMART APEX diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Cell refinement and data reduction were carried out with the use of the SAINT package [13]. The structures were solved by direct methods with the program SHELXS [13] and refined by full-matrix least-squares techniques with SHELX-97 [14]. Hydrogen atoms were included in calculated idealized positions and constrained with the use of a riding model. The final models involved anisotropic displacement parameters for all non-hydrogen atoms. The drawings were created with the Diamond program by Crystal Impact GbR. [15]. CCDC-626507 contains the supplementary crystallographic data for this paper.

Synthesis of $(\text{HDMBG})_2(\text{NO}_3)(\text{ClO}_4)$: To a solution of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.809 g, 5mmoles) in ethanol (50 mL) was slowly added $\text{DMBG} \cdot \text{HNO}_3$ (1.920 g, 10 mmoles) under continuing stirring and heating at 50°C. The reaction mixture was then stirred at 50°C for 2 h until a pink solution was formed. This solution was left at room temperature for several weeks until a brown precipitate was formed. The solution resulted after the precipitate removed was left at slow evaporation until colourless crystals were formed. The crystals were filtered off and washed several times with a small volume of cold ethanol, ethylic ether and air-dried. Crystals suitable for X-ray determination were obtained by ethanol recrystallization. *Analysis found*: C, 22.74; H, 5.78; N, 36.59 %; *requires for* $\text{C}_8\text{H}_{24}\text{ClN}_{11}\text{O}_7$: C, 22.78; H, 5.73; N, 36.53 %. IR (KBr pellet), cm^{-1} : $\nu_{\text{as}}(\text{NH}_2)$, 3335vs, 3286vs; $\nu(\text{NH})$, 3112vs, 3099vs; $\nu_{\text{s}}(\text{NH}_2)$, 3014vs; $\nu(\text{C}=\text{N})$, 1628vs; $\delta_{\text{as}}(\text{NH}_2)$, 1587s; $\delta_{\text{s}}(\text{NH}_2)$, 1495m; $\nu_3(\text{NO}_3)$, 1375vs; $\nu(\text{C}-\text{N})$, 1262w; $\nu_3(\text{ClO}_4)$, 1079vs, $\nu_2(\text{NO}_3)$, 839w; $\rho(\text{CH}_3)$, 725w; $\nu_4(\text{ClO}_4)$, 625s.

3. Results and discussion

Starting from N,N-dimethylbiguanidium nitrate and using manganese (II) perchlorate an interesting mixed derivative $(\text{HDMBG})_2(\text{NO}_3)(\text{ClO}_4)$ was isolated and characterised by elemental analysis and IR spectroscopy. The recrystallised fresh crystals from ethanol were consistent with the same formula.

3.1. Infrared spectra

The IR spectrum of compound (see experimental part) reveal the characteristic bands of N,N-dimethylbiguanidium cation [5]. All the bands assigned to the stretching vibrations of amine and imine groups are significantly towards lower wavenumbers in comparison with the spectra of the N,N-dimethylbiguanidium hydrochloride. This behaviour suggests that the

hydrogen bonds with anions are stronger for this derivative. In the ranges characteristic for nitrate and perchlorate anions appear intense bands characteristic for the free anions displaying C_{3v} and T_d symmetry respectively [16]. This indicates that all oxygen atoms of the anions are involved in similar hydrogen bonds with N,N-dimethylbiguanidium cations.

3.2. The X-ray crystal structure

Three-dimensional structure of $(\text{HDMBG})_2(\text{NO}_3)(\text{ClO}_4)$ was determined by single-crystal X-ray diffraction and a summary of crystal data, data collections and refinement is given in Table 1.

Table 1 Summary of crystal data for $(\text{HDMBG})_2(\text{NO}_3)(\text{ClO}_4)$

Color/shape	Color less/block
Empirical formula	$\text{C}_8 \text{H}_{24} \text{Cl} \text{N}_{11} \text{O}_7$
Formula weight	421.83
Temperature	293(2) K
Crystal system	Monoclinic
Space group	C2/c
	$a = 7.147(6) \text{ \AA}$
	$\alpha = 90^\circ$
	$b = 25.46(2) \text{ \AA}$
	$\beta = 98.243(14)^\circ$
	$c = 10.951(9) \text{ \AA}$
	$\gamma = 90^\circ$
Unit cell dimensions	
Volume	$1972(3) \text{ \AA}^3$
Z	4
Calculated density	1.421 mg/m^3
Absorption coefficient	0.249 mm^{-1}
F(000)	888
Goodness-of-fit on F^2	1.081
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0682$, $wR2 = 0.1515$
R indices (all data)	$R1 = 0.0901$, $wR2 = 0.1633$
Largest difference peak and hole	0.234 and $-0.324 \text{ e. \AA}^{-3}$

The selected bond distances and angles are shown in Table 2.

Table 2 Selected bond distances and angles for $(\text{HDMBG})_2(\text{NO}_3)(\text{ClO}_4)$

Bond distances (\AA)		Angles ($^\circ$)	
N(1)-C(3)	1.333(4)	N(5)-C(4)-N(4)	117.5(3)
C(4)-N(5)	1.326(4)	N(5)-C(4)-N(3)	118.1(3)
C(4)-N(3)	1.338(3)	N(4)-C(4)-N(3)	124.2(3)
C(3)-N(2)	1.337(4)	N(1)-C(3)-N(2)	118.8(3)
C(3)-N(3)	1.341(4)	N(1)-C(3)-N(3)	118.4(3)
O(3)-N(6)	1.234(4)	N(2)-C(3)-N(3)	122.5(3)
O(4)-N(6)	1.250(3)	C(4)-N(3)-C(3)	121.7(2)
O(1)-Cl(1)	1.402(3)	O(3)-N(6)-O(4)	120.24(17)
O(2)-Cl(1)	1.410(3)	O(4)-N(6)-O(4a)	119.5(3)
		O(1a)-Cl(1)-O(1)	110.0(3)
		O(1a)-Cl(1)-O(2)	109.6(2)
		O(2a)-Cl(1)-O(2)	107.4(3)

The molecular structure of $(\text{HDMBG})_2(\text{NO}_3)(\text{ClO}_4)$ is depicted in Fig. 1. The C-N bonds of each HDMBG unit in the range of 1.326(4)-1.341(4) are longer than a double bond indicating a π -electron density delocalisation along the biguanide group [17].

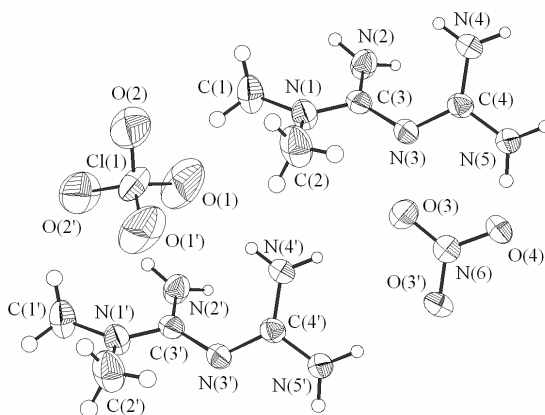


Fig. 1 General view of the molecular structure for $(DMBG)_2(NO_3)(ClO_4)$ showing 30% probability displacement ellipsoids and the atom numbering scheme. Hydrogen atoms are shown as small spheres of arbitrary radii.

The packing diagram shows N,N-dimethylbiguanidinium units connected by two N(5)-H...N(3) hydrogen bonds. This hydrogen bonds developing generate an elongated hexagon, pattern observed also for $(HDMBG)(NO_3)$ [12].

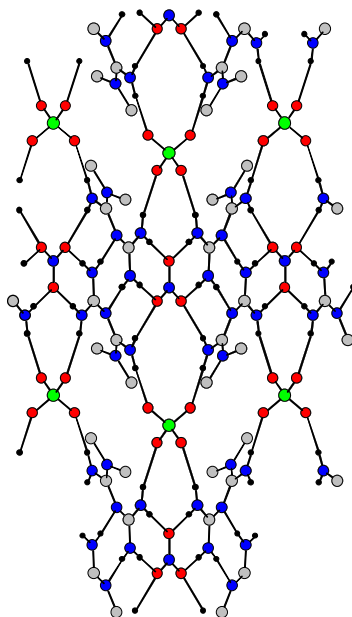


Fig. 2 Crystal arrangement with the intermolecular interactions viewed along the a axis for $(DMBG)_2(NO_3)(ClO_4)$

These units are held together in the crystal by a number of intermolecular N-H...O interactions. Each nitrate anion is involved in six such interactions while each perchlorate

realises four connections. The anions involvement in non-equivalent hydrogen interactions generate a slightly distortion of nitrate from a regular triangle with O-N-O angles varying between 119.5(3) and 120.24(17)°. The same behaviour can be noticed for perchlorate for which the distortion from a regular tetrahedron is revealed by the O-Cl-O angles that vary from 107.4(2) to 110.0(3)°.

4. Conclusion

A new derivative (HDMBG)₂(NO₃)(ClO₄) was synthesised and fully characterized by single crystal X-ray diffraction.

IR spectrum is consistent with N,N-dimethylbiguanidium cation as well as nitrate and perchlorate anions involved in the same hydrogen interactions.

Compound crystallises in the monoclinic group and displays a packing diagram similar with N,N-dimethylbiguanidium nitrate derivative.

REFERENCES

1. Olar, R., Badea, M., Marinescu, D., Lazar, V. and Balotescu, C. (2007) *J. Therm. Anal. Calor.* **88**, 323.
2. Wood, A.J.J., Bailey C.J. and Turner, R.C. (2003) *New England J. Med.* **334**, 574.
3. Pignard, P. (1962) *Ann. Biol. Clin.* **20**, 325.
4. Siest, G., Roos, F. and Gabou, J.J. (1963) *Bull. Soc. Pharm. Nancy* **58**, 29.
5. Olar, R., Badea, M., Cristurean, E., Lazar, V., Cernat, R. and Balotescu, C. (2005) *J. Therm. Anal. Calor.* **80**, 451.
6. Olar, R., Badea, M., Cristurean, E., Parnau, C. and Marinescu, D. (2006) *J. Therm. Anal. Calor.* **84**, 53.
7. Olar, R., Badea, M., Grecu, M.N., Marinescu, D., Lazar, V. and Balotescu, C. (2008) *J. Therm. Anal. Calor.* **92**, 239-43.
8. Olar, R., Badea, M., Marinescu, D., Iorgulescu, E.E., Frunza, E., Lazar, V. and Chifiriuc, C. (2010) *J. Therm. Anal. Calor.* **99**, 815.
9. Olar, R., Badea, M., Marinescu, D., Chifiriuc, C., Bleotu, C., Grecu, N., Iorgulescu, E.E., Bucur, M., Lazar, V. and Finaru, A. (2010) *Eur. J. Med. Chem.* **45**, 2868.
10. Olar, R., Badea, M., Marinescu, D., Chifiriuc, C., Bleotu, C., Grecu, N., Iorgulescu, E.E. and Lazar, V. (2010) *Eur. J. Med. Chem.* **45**, 3027.
11. Hariharan, M., Rajan, S.S. and Srinivassan, R. (1989) *Acta Cryst.* **C45**, 911.
12. Zhu, M., Lu, L. and Yang, P. (2003) *Acta Cryst.* **E59**, o586.
13. ***Bruker (2001). SMART (Version 5.625), SAINT+ (Version 6.0), SHELXTL (Version 6.10) and SADABS (Version 2.03), Bruker AXS Inc., Madison, Wisconsin, USA.
14. ***Sheldrick, G.M. (1997) *SHELXL-97*, University of Gottingen, Germany.
15. ***DIAMOND – Visual Crystal Structure Information System, CRYSTAL IMPACT Postfach 1251, D-53002 Bonn, Germany, 2001.
16. Hathaway, B.J. (1987) **Comprehensive Coordination Chemistry**, Vol. 2, G. Wilkinson, R.D. Gillard, J.A. McCleverty, Eds.; Pergamon Press, Oxford, U.K..
17. Yurkanis Bruice, P. (2001) **Organic Chemistry**, 3rd Ed., Prentice Hall Inc., Pearson Education.