International Journal of Current Research in Chemistry and Pharmaceutical Sciences
www.ijcrcps.com Volume 1 Issue: 4 2014 Pages:93-98
(p-ISSN: 2348-5213; e-ISSN: 2348-5221)

RESEARCH ARTICLE

SYNTHESIS AND CRYSTAL STRUCTURE OF (BIS [(2-AZANIUMYL-3-METHYLBUTANOYL) OXY](Λ^2-BROMANIDYL)FERRIO)-Λ^2-BROMANIDE

M. RADHA RAMANAN[1], P. GEETHA[2], R. RADHAKRISHNAN[3], V. CHITHAMBARAM[2] AND B. GUNASEKARAN[4*]

[1]Department of Physics, Arasu Engineering College, Kumbakonam, Tamil Nadu, India.
[2]Research Centre Physics, Dhanalakshmi College of Engineering, Tambaram, Chennai-600 059 Tamil Nadu, India.
[3]PG & Research Department of Physics, Jamal Mohamed College, Tiruchirappalli, Tamil Nadu, India.
[4]Department of Physics & Nano Technology, SRM University, SRM Nagar, Kattankulathur, Kancheepuram Dist, Chennai-603 203 Tamil Nadu, India.

*Corresponding Author: *gunasekaran.b@ktr.srmuniv.ac.in; bguna_sekaran77@yahoo.co.in*

Abstract

The crystal structure of the title compound has been determined by means of X-Ray diffraction. The compound crystallizes in the triclinic space group *P1* with a = 6.173 (2) Å, b = 8.202 (3) Å, c = 9.613 (4) Å and α = 76.217 (2), β = 83.006 (2), γ = 68.474 (3) º. The terminal methyl groups of L-valine moiety is disordered over two positions with site occupancies of 0.51/0.49 and 0.63/0.37. The crystal packing of the compound is controlled by weak intermolecular C-H…O and N-H…O and N-H…Br interactions.
.

Keywords: single-crystal X-ray study, L-valine, disorder, R factor = 0.037.

Introduction

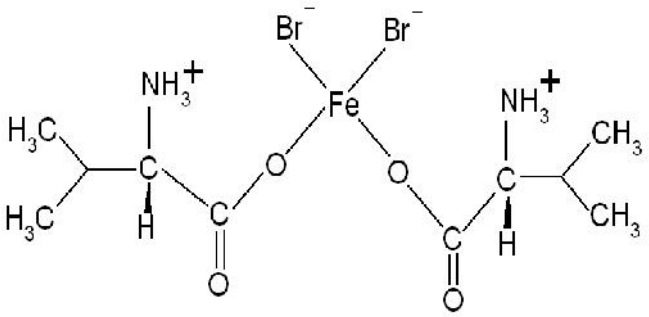
Amino acids play central role as building blocks of proteins. Amino acids act not only as the building blocks in protein synthesis but also play a significant role in metabolism. The specific metabolic role of amino acids includes the biosynthesis of polypeptides, proteins and synthesis of nucleotides (Barrett, 1988). The oxidation of amino acids is of interest as different oxidation products are obtained using different oxidants (Laloo and Mahanti, 1990; Annapurna et al., 2008). Valine is one of the 20 proteinogenic (Ambrogelly et al., 2007) amino acid. L-Valine is an essential amino acid classified as non-polar, and forms active sites of enzymes and helps in maintaining proper conformation by keeping them in proper ionic states and wide applications in pharmaceutical and food industry (Bartek et al., 2010). Hence, oxidation of L-Valine may help in understanding some aspects of enzyme kinetics. Valine is a branched-chain amino acid (BCAAs) along with leucine and isoleucine. It is named after the plant valerian. In sickle-cell disease (Platt et al., 1994), valine substitutes for the hydrophilic amino acid glutamic acid in hemoglobin (Bruce et al., 2006). Because valine has large aliphatic hydrophobic side chains (Wang and L. Jiang, 2007), the hemoglobin does not fold correctly. It promotes muscle growth and tissue repair. Many workers (Andreoli, et al., 1984; Saxena and Dhawan, 1983) have studied biologically active metal complexes of amino acids which are important in analytical, biochemical and pharmaceutical fields (Patel, et al., 1996; Khan and P.L. Sahu, 2000; Singh, et al., 1995) and attracted wide attention in different fields of

research. Mixed ligand complexes of transition metals with many amino acids have been studied by many workers (Singh et al., 2008; Khanam and F. Khan, 2008; Prakash et al., 2007; Zine, 2006; Shakoor and Hussain, 2007; Reddy and Radhika, 2005; Jangid and Chandel, 2007). The importance of amino acids in NLO applications is due to the fact that all the amino acid has chiral symmetry and crystallizes in noncentro-symmetric space groups (Bhat and Dharmaprakash, 2002).

Experimental

The 0.585g 2-amino-3-methylbutanoic acid (5 mmol) and 1.477g Iron (III) bromide (5 mmol) were dissolved in deionized water. The solution was agitated with a magnetic stirring device for twelve hours continuously and filtered after complete dissolution of the starting materials. The prepared solution was allowed to dry at room temperature and the crystals were obtained by slow evaporation technique.

Scheme



X-Ray Structure Determination

Single crystal X-ray diffraction data for the compound at room temperature was collected by Bruker Kappa diffractometer with Mo Kα radiation using ω/2θ scan mode. SMART APEX2 CCD area detector with Mo Kα radiation and ω scan mode was applied to obtain an accurate unit cell parameters and orientation matrix within the least-square fit of several high angle reflections in the ranges $2.18^{o} < \theta < 25.0^{o}$. Cell refinement and data reduction were carried out using SAINT. A total of 9788 reflections were collected, resulting in 3084 independent reflections of which 2895 had $I > 2\sigma(I)$. The intensities for Lorentz and polarization effects and absorption corrections were corrected by using SADABS (Sheldrick, 1996). The structure of compound was solved by direct method procedure as implemented in SHELXS97 (Sheldrick,1997) program. The full matrix least square refinement using SHELXL97 program was used to include the position of all non hydrogen atoms. The thermal parameters for each atom were assigned a value of 0.05 (U's) in the initial stage and refinement was followed. The initial scale factor was pegged at 1.0. Thereafter the anisotropic refinement for a few cycles of full matrix least square was continued. At this stage the positions of all hydrogen's were geometrically fixed at calculated positions and they were allowed to ride on the corresponding non hydrogen atoms. The minimum and maximum value of residual electron density was -0.65, 0.92 $e.Å^{-3}$ and the final R-factor was 0.037. Crystallographic data of the compound is summarized in Table 1.

Results and Discussion

Fig. 1 shows the ORTEP plot of the molecule drawn at 30% probability ellipsoid level with atom numbering scheme. Fig. 2 shows the packing of compound viewed down 'a' axis. The geometric parameters of the title molecule agree well with reported similar structure (Merola et al., 2014). In this compound terminal methyl groups of L-valine moiety is disordered over two positions with site occupancies of 0.51/0.49 and 0.63/0.37. The site occupancy factor of disordered C atoms were redefined as C5 = 0.51 (8), C5' = 0.49 (8) and C9 = 0.63 (3), C10 = 0.63 (3), C9' = 0.37 (3) and C10' = 0.37 (3) during anisotropic refinement. For the molecule is disordered, during refinement SIMU and SADI were used for the atoms C3, C4, C5, C5' C8, C9 C10, C9' and C10'. The crystal packing is controlled by weak intermolecular C-H...Br, N-H...O and N-H...Br interactions. Table 2 summarizes the selected geometrical parameters of the compound and Table 3 gives the Hydrogen bond data of the compound.

Conclusions

Amino acid metal complexes and their derivatives are of great importance because of their biochemical and pharmacological properties. Valine is an essential amino acid and it can chelate to metal ions via its amino N atom and carboxylate O atom. The structure fused with Iron (IV) and L-Valine moiety. The terminal methyl group of valine moiety is disordered over two positions. In the crystal weak intermolecular C-H…O, N-H…O and N-H…Br interactions are observed.

Table. 1 Crystal data, data collection and structure refinement

Formula	$C_{10}H_{22}Br_2FeN_2O_4$
Formula weight	449.97
Crystal system	Triclinic
Space group	*P1*
T (K)	296(2)
a (Å)	6.173(3)
b (Å)	8.202(4)
c (Å)	9.613(4)
α (°)	76. 217(2)
β(°)	83.006(2)
γ (°)	68. 474(2)
V (Å^3)	439.47(3)
Z	1
D_x (g cm^{-3})	1.700
F(000)	224
μ (mm^{-1})	5.41
Crystal size (mm)	0.35 0.32 0.30
Θ range (°)	2.2–25.0
hkl range	-7 ≤ h ≤ 7
-9 ≤ k ≤ 9	
-11 ≤ l ≤11	
Reflections	
Collected	9788
Unique (R_{int})	3084 (0.037)
With [I>2σ(I)]	2895
Number of parameters	203
R(F) [I>2σ(I)]	0.037
wR(F^2) [I>2σ(I)]	0.105
R(F) [all data]	0.039
wR(F^2) [all data]	0.096
Goodness of fit	1.08
Max/min Δρ (e Å^{-3})	0.92/-0.65

Table. 2 Selected geometrical parameters (Å, °) with su's in parentheses

C1-O1	1.211(8)		
C1-O2	1.266(8)	O1-C1-O2	127.2(6)
C1-C2	1.513(8)	O4-C6-O3	127.3(6)
C2-N1	1.480(8)	C1-O2-Fe1	130.8(5)
C6-O4	1.201(8)	C6-O3-Fe1	131.6(4)
C6-O3	1.261(8)	O2-Fe1-O3	95.7(2)
C6-C7	1.529(8)	O2-Fe1-Br1	110.3(2)
C7-N2	1.468(8)	O3-Fe1-Br1	116.1(2)
O2-Fe1	1.944(5)	O2-Fe1-Br2	114.7(2)
O3-Fe1	1.948(5)	O3-Fe1-Br2	108.5(2)
Fe1-Br1	2.3690(11)	Br1-Fe1-Br2	110.93(4)
Fe1-Br2	2.3780(11)		

Table. 3 Non-Bonded interactions and possible hydrogen bonds (Å, º)

D-H...A	D-H	H...A	D...A	DHA
C2-H2...Br1i	0.98	3.03	3.947(6)	156.7
C7-H7...Br2ii	0.98	3.03	3.935(6)	154.3
N1-H1A...O4i	0.89	2.24	2.961(8)	137.7
N1-H1A...Br2iii	0.89	2.96	3.404(5)	112.7
N1-H1B...O1iii	0.89	2.04	2.865(7)	154.2
N1-H1C...Br1iii	0.89	2.70	3.472(5)	145.4
N2-H2A...Br2iii	0.89	2.69	3.490(6)	150.4
N2-H2B...O1ii	0.89	2.37	2.996(9)	127.1
N2-H2B...Br1iii	0.89	2.89	3.452(6)	122.3
N2-H2C...O4iii	0.89	2.02	2.856(7)	156.7

Symmetry Equivalent position:

(i) -1+x, 1+y, z (ii) x, -1+y, z (iii) -1+x, y, z

Fig. 1 ORTEP plot of the compound drawn at 30% probability

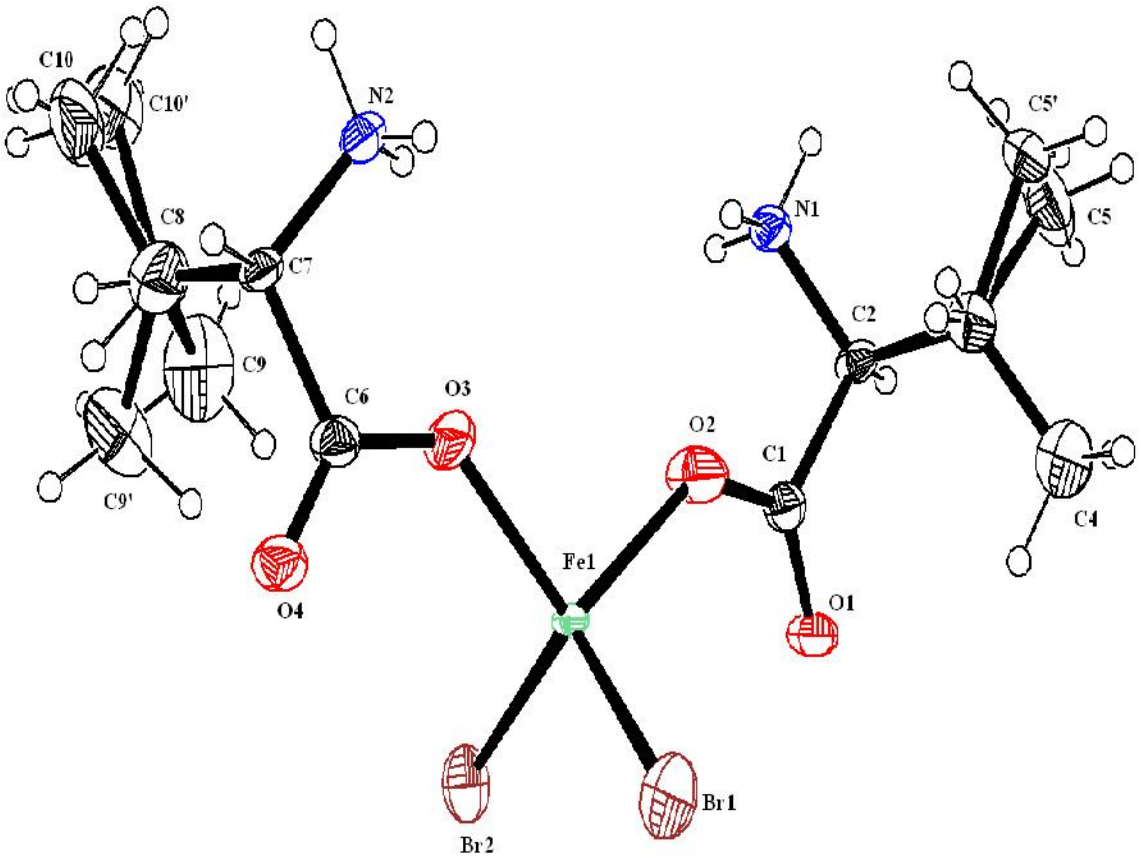
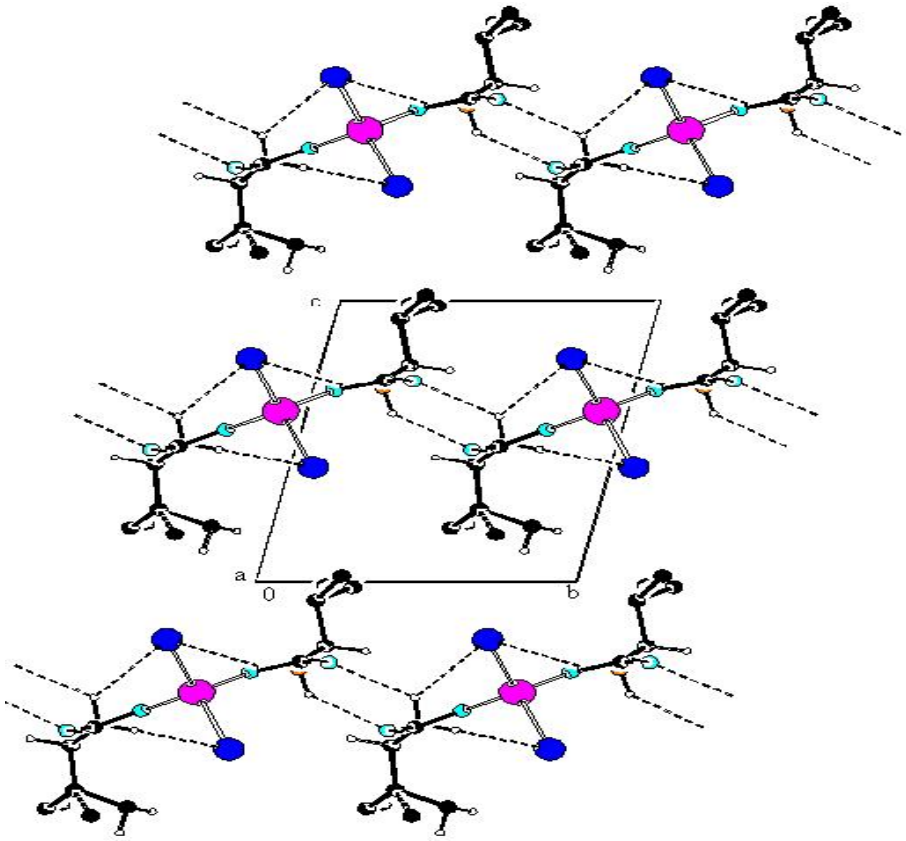


Fig. 2 Packing of the compound viewed down 'a' axis. Hydrogen bonds are shown as dashed lines.



Acknowledgements

The authors thank Dr. Babu Vargheese, SAIF, IIT, Madras, India, for his help in collecting the X-ray intensity data and Dr. A. Thiruvalluvar, PG Research Department of Physics, Rajah Serfoji Government College (Autonomous), Thanjavur, Tamil Nadu, India for his kind suggestion and constant support.

References

Ambrogelly, A., S. Palioura, and D. Soll. 2007. Natural expansion of the genetic code. Nat Chem Biol 3:29, 35.

Andreoli R., L. Benedeti, G. Grandi,Baltistuzzi and G. Gavioli. 1984. Elecrochem Acta, 9: 227(A)

Annapurna, N., A. K. Kumar, P. Vani and G. J. Nageswara Rao. 2008. Indian Chem Soc. 85: 542.

Barrett G. C., 1998. Amino Acids, Peptides and Proteins, (Royal Society of Chem, UK), P.29.

Bartek T., B. Blombach, E. Zönnchen, P. Makus, S. Lang, B. J. Eikmanns, and M. Oliges.2010. Biotechnol. Prog., 26: 361-371.

Bhat, M.N and S.M. Dharmaprakash. 2002. J.Cryst. Growth 235: 511.

Bruce, D., K. M. Sidell, and O. Brien. 2006. J Exp Biol . 209:1791–1802.

Jangid K. R. and C. P.S. 2007. Chandel, Journal of Ultrachemistry, 19.

Khan, F. and P.L. Sahu. 2000. Ultra Scientist Phys.Sci. 12: 106.

Khanam, A., and F. Khan. 2008.J. Indian Chem. Soc,85:89-91.

Laloo, D., and M. K. Mahanti. 1990. J. Chem. Soc. Dalton. Trans, 311.

Merola, J. S., C. Slebodnick, M. Berg and M. K. Ritchie. 2014. Acta Cryst, E70, m82-m82.

Patel, R.N., H.C. Pandey and K.B. Pandey. 1996. Bull. Electrochem. 12:612.

Platt, O. S., D. J. Brambilla, W. F. Rosse, P. F. Milner, O. Castro, and M. H. Steinberg. 1994. N Engl J Med. 330:1639–1644.

Prakash, D., R. P. Suman, A. K. Gupta and S.Kumar. 2007. Oriental Journal of Chemistry. 23..

Reddy, P.R. and M. Radhika. 2005. J. Chem. Sci,117(3): 239-246..

Saxena, R.S. and S.K. Dhawan. 1983. Trans SAEST.18: 131(A) .

Shakoor, M. A .and S. Hussain. 2007. Asian Journal of Chemistry, 19: 311-314.

Sheldrick, G. M. 1997. SHELXS97 & SHELXL97 University of Gottingen Germany.

Sheldrick, G. M. 1996. SADABS University of Gottingen Germany.

Singh, B.K.,.C.L. Jain and R.S. Sindhu, Trans.SAEST. 30:4.

Singh, M.K., A. Das, R. Laskar and B. Paul. 2008. J.Indian Chem. Soc. 85:485-490..

Wang, S. and L. Jiang. 2007. Adv Mater 19, 3423–3424.

Zine, A.M. 2006. Asian Journal of Chemistry, 18(4):2902-2906.

